ASSESSMENT

OF THE

POTENTIAL FOR COMMERCIALIZATION

OF A

LOW SEVERITY CATALYTIC HYDROGENATION PROCESS

FOR

MIDDLE DISTILLATE UPGRADING

BY:

RTM ENGINEERING LTD.

DECEMBER, 1987

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FINAL REPORT

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TABLE OF CONTENTS

		Page
	Abstract	vi
	Resumé	vii
1.	Synopsis	1-1
	1.1 Introduction	1-1
	1.2 Setting	1-1
	1.2.1 Current Middle Distillate Aromatic Concerns	1-1
	1.2.2 Future Concerns	1-2
	1.2.3 Refinery Capabilities	1-2
	1.3 Refiner Alternates	1-3
	1.3.1 Overview	1-3
	1.3.2 Aromatic Saturation	1-3
	1.4 Typical Canadian Feedstocks	1-5
	1.5 Comparison	1-6
	1.5.1 Preamble	1-6
	1.5.2 Conventional NiMo	1-6
	1.5.3 Nickel	1-7
	1.5.4 Cost Comparison	1-8
	1.5.5 Nickel Without Prior Hydrotreating	1-9
	1.6 Conclusions	1-10
	1.7 Recommendations	1-10
2.	Introduction	2-1
	2.1 Terms of Reference	2-1
	2.2 Methodology	2-1
	2.3 Aromatics	2-2
	2.4 Acknowledgements	2-3
3.	Process Market Assessment	3-1
	3.1 Preamble	3-1
	3.2 Existing Refineries	3-2
	3.3 Crude Oils	3-5
	3.3.1 General	3-5
	3.3.2 Canadian Crude Type Forecasts	3-7
	3.3.3 Impacts of Syncrude Type Synthetic Crude Oils	3-10
	3.4 Specification Changes	3-10
	3.5 Product Demands	3-13
	3.5.1 General	3-13
	3.5.2 Impact Analysis	3-13
	3.6 Refinery Technology Changes	3-17
	3.6.1 General	3-17
	3.6.2 Middle Distillate Options	3-18
	3.7 Process Market	3-20
	3.7.1 General	3-20
	3.7.2 Short Term	3-20
	3.7.3 Long Term	3-21
	3.7.4 Summary	3-22

4. Aromatic Saturation Processes 4-1
4.1 Preamble 4-1
4.2 Hydroprocessing Alternate 4-2
4.2.1 Type I Precious Metal Sulphide Catalysts 4-2
4.2.2 Type II Other Precious Metal Catalysts 4-2
4.2.3 Type III Nickel Catalysts 4-3
4.2.4 Type IV Miscellaneous Catalysts 4-3
4.2.5 Type V Conventional NiMo and NiW Catalysts 4-4
4.2.6 Type VI Mild Middle Distillate Hydrocracking Processes 4-5
4.3 Adsorbents 4-6
4.4 Saturation Process Selection Today 4-7
5. Process Comparison 5-1
5.1 Preamble 5-1
5.2 Feedstocks 5-1
5.2.1 General 5-1
5.2.2 Prior Processing in Blend and Light Cycle Oil Cases 5-3
5.2.3 Suncor Kerosene 5-3
5.2.4 Syncrude Middle Distillate 5-4
5.2.5 Blend 5-5
5.2.6 Light Cycle Oil 5-6
5.3 Facility and Cost Bases 5-6
5.3.1 Integration with Existing Facilities 5-6
5.3.2 Capital Costing 5-7
5.3.3 Operations Costing 5-7
5.4 Conventional Route 5-8
5.4.1 General 5-8
5.4.2 Process Description 5-9
5.4.3 Special Operations 5-12
5.4.4 Stream Factor 5-12
5.5 Nickel Saturation Route 5-13
5.5.1 Process Parameters 5-13
5.5.2 Guard Beds 5-15
5.5.3 Saturation Catalyst 5-16
5.5.4 Objective Achievement 5-17
5.5.5 Process Design 5-18
5.5.5.1 Hydrodesulphurization 5-18
5.5.5.2 Saturation Section 5-19
5.5.5.3 Heat Recovery 5-19
5.5.6 Stream Factor 5-20
5.6 Yield Data 5-20
5.7 Capital Costs 5-20
5.7.1 Comparison 5-20
5.7.2 Platinum Based Reference Point 5-21
5.8 Operating Costs 5-21
5.9 Comparison Summary 5-22
5.10 Saturation Only 5-23
5.10.1 Preamble 5-23
5.10.2 Capital Cost 5-23
5.10.3 Operating Cost Breakout 5-24
5.10.4 Stand Alone Saturation Unit 5-24
5.11 Nickel Catalysts Industry 5-26

6. Conclusions 6-1
6.1 Canadian Refiner Needs 6-1
6.2 Nickel Catalyst Competitiveness 6-2
6.3 New Data Needs 6-2
7. Recommendations 7-1
7.1 General 7-1
7.2 Competitive Routes 7-1
7.3 Nickel Catalyst Specific 7-1

Bibliography and Personal Communications

Appendix A
Nickel Catalyst Hazards

List of Tables

Table 1.5.2-1	Conventional NiMo Paramters	1-6
Table 1.5.3-1	Nickel Saturation Parameters	1-7
Table 1.5.4-1	Cost Comparison	1-9
Talbe 3.2-1	Selected Canadian Refinery Data	3-4
Table 3.3.1-1	Selected Crude Assay Data	3-6
Table 3.3.2-1	Refinery Crude Feedstock Sourcing	3-8
Table 3.3.2-2	New Frontier Crude Penetration in Conventional Refineries	3-8
Table 3.3.2-3	Crude Oil Type Forecast for Ontario, Prairie, B.C.	3-9
Table 3.3.2-4	S.C.O. Penetration	3-9
Table 3.4-1	Preliminary Estimate of Canadian Middle Distillate Specification Changes	3-12
Table 3.5.1-1	Product Demand Data	3-14
Table 3.5.1-2	Net Product Transfers in 1985 & 1986	3-15
Table 3.5.2-1	Overall Product Demand Changes	3-16
Table 3.6.2-1	Cetane Improver Cost	3-19
Table 5.2.1-1	Feedstock Qualities	5-2
Table 5.4.1-1	Conventional Route Paramters	5-8
Table 5.5-1	Nickel Route Parameters	5-13
Table 5.6-1	Yield and Utility Consumption Data	5-20
Talbe 5.7.1-1	Capital Cost Estimates	5-21
Table 5.8-1	Operating Cost Estimates	5-22
Table 5.9-1	Comparison	5-23
Table 5.10.2-1	Nickel Route Capital Cost Breakdown	5-23
Table 5.10.3-1	Nickel Route Operating Cost	5-24
Table 5.10.4-1	Single Stage Nickel Saturation Unit Costs	5-26

List of Figures

Figure 1.5.2-1	Simplified Diagram of Conventional NiMo Saturation	1-7
Figure 1.5.3-1	Simplified Diagram of Nickel Saturation Route	1-8
Figure 1.6-1	Approximate Economic Fits Middle Distillate Saturation Process	1-11
Figure 3.2-1	Simplified Outline of Typical Canadian Refinery	3-2
Figure 4.2.6-1	Variation of Aromatic Carbon with Cetane Number - A Comparison of Synthetic Crudes With LCO	4-5
Figure 5.4.2-1	Conventional Hydrotreater Schematic	5-10
Figure 5.5-1	Nickel Saturation Unit Schematic	5-14
Figure 5.10.4-1	Stand Alone Saturation System	5-25

ABSTRACT

Possible mid 1990's specifications limiting the aromatic content of Canadian jet and diesel fuels will severely strain Canadian refiners. Increasing use of synthetic crude oils will worsen this problem. This study shows that a low severity hydrogenation process has possible commercial applications in both the short term (1992) and long term (2005). CANMET has done extensive test work with conventional high severity aromatic saturation catalysts and recently has been developing a low severity supported nickel catalyst route. The study compares these two routes for four feedstocks representing Canadian applications - synthetic crude middle distillates from each of Suncor Inc. and Syncrude Canada Ltd., a blend of conventional crude diesel and light cycle oil from catalytic cracking and, lastly, light cycle oil. The study shows capital costs of both routes to be approximately equal, but the nickel catalyst route has marginally higher operating costs. At this time both process routes studied are still very expensive. The development of a sulphur tolerant nickel catalyst along with regenerability would greatly improve the economics of aromatic saturation generally.

RESUME

L'entrée en vigueur, possiblement vers le milieu des années 90, des spécifications limitant la teneur en aromatiques du carburéacteur et du combustible diésel produits au Canada causera de nombreux problémes aux raffineurs canadiens. Ces problémes s'aggraveront en raison de l'utilisation accrue de brut synthétique. La présente étude démontre qu'il est possible d'appliquer à l'échelle commerciale, soit à court terme (1992) ou à long terme (2005), un procédé d'hydrogénation à basse sévérité. CANMET a effectué des essais exhaustifs à haute sévérité au moyen de catalyseurs de type courant pour la saturation des aromatiques et a récemment mis au point un procédé à basse sévérité utilisant un catalyseur de nickel. Les deux procédés sont étudiés et comparés au moyen de quatre charges d'alimentation susceptibles d'étré utilisées au Canada. Ces charges d'alimentation comprennent des distillats moyens de brut synthétique provenant respectivement de Suncor Inc. et de Syncrude Canada Ltd., un mélange de diesel brut classique et de coupe légére recyclée obtenue par craquage catalytique et enfin, de l'huile légére recyclée. L'étude démontre que le coût en capital des deux tracés est à peu prés le méme mais que les frais d'exploitation du catalyseur à base de nickel sont plus élevés. Le développement d'un catalyseur de nickel ayant une tolérance au soufre et la possibilité de regénération améliorerait considérablement l'aspect économique de la saturation aromatique.

1. SYNOPSIS

1.1 INTRODUCTION

This study considers the competitive aspects of a nickel based route to the saturation of aromatics in Canadian middle distillates. It is based upon laboratory and pilot work by the CANMET/Energy Research Laboratories (ERL) of the federal Department of Energy Mines and Resources (EMR) relative to both "conventional" high pressure hydrogenation and comparatively low pressure nickel catalyst hydrogenation. Supporting data were drawn from catalyst developers, catalyst vendor contracts and the technical literature.

CANMET studied the nickel route as one approach to offset the high and rising cost of platinum used in other low pressure processes and as an alternate to the high pressure conventional nickel molybdenum and nickel tungsten catalyst routes. The CANMET work to date has used catalysts currently commercially available.

This study investigates the Canadian setting for middle distillate aromatic saturation to note relative economics and prospective applications, and to develop recommendations for future research and development activities.

1.2 SETTING

1.2.1 Current Middle Distillate Aromatic Concerns

Currently, Canadian refineries have problems in the following areas:

Aromatics - Jet A - The present limit of 25 percent by volume of aromatics maximum and/or a smoke point of at least 18, restrict the intake of synthetic crude oils (S.C.O.) at refineries producing Jet A due to the 25 plus aromatic content of S.C.O. kerosene fractions and their poor - 16 to 18 - smoke point.

Diesel Cetane - S.C.O. diesel fractions have cetane numbers between 30 and 35, but the specification for diesel fuel is 40 minimum. Refineries in western Canada must also blend very low cetane (25 or so) light cycle oil (from catalytic cracking) into diesel fuel at 15 to 20 percent of the total. Ontario and Quebec refineries are affected to a lesser extent as they have light fuel oil and residual fuel oil markets that can absorb all or part of the light cycle oil.

- Use of cetane improver chemicals becomes very expensive over a 5 or 6 number increase but is generally adequate, at least in the near term.

- As only two refineries now have specific facilities to improve the quality of their diesel fuel, most refineries are

quite constricted in their use of S.C.O. for diesel production.

1.2.2 Future Concerns

All forecasts indicate more S.C.O. production and use in the future. Some new domestic crude oils, such as those from the Beaufort Sea, also are likely to exceed currently used crudes in aromatic content and to be lower in cetane. At the same time, the light fuel oil market in eastern Canada is projected to decline, decreasing that outlet for light cycle oil, while at the same time Jet A markets rise across the country along with diesel. Future S.C.O. may be less aromatic than current versions due to added processing in upgrading.

The middle distillate yield of current synthetic crude oils and of Beaufort Sea crudes is above market demands and some hydrocracking to naphtha may be needed as their use increases, despite slowly declining gasoline to middle distillate sales ratios.

In order to meet 1995 U.S. diesel engine emission standards it may be necessary to lower the aromatic content of diesel fuels, and Canada will very likely follow a U.S. lead in this regard. A 20 volume percent aromatic limit has been suggested in the U.S., but sufficient test work has not been done to properly correlate aromatic content and other fuel parameters with emissions and emissions to arrive at any scientific conclusion. Such data will not be available until the middle of 1989. Here, we assume the odds as being about 50 percent for a diesel specification controlling aromatic content at a level in the order of 25 percent.

Reduction of the sulphur specifications for diesel fuels are expected in the next five years, but it appears unlikely that resulting hydrotreating facilities will have any significant aromatic reduction or cetane improvement capabilities.

1.2.3 Refinery Capabilities

As noted, only two Canadian refineries have any significant aromatic saturation capability. (Two small units at other refineries reduce the aromatic content of kerosene fractions used in solvents, but these are insignificant even at the individual refinery level.) Another unit is under construction relative to heavy crude processing in Regina, and Syncrude has a similar middle distillate hydrotreater under construction which will process a portion of their middle distillates.

Imposition of a diesel aromatic specification in the 20 to 25 percent by volume range would necessitate aromatic saturation units at about 12 Canadian refineries. New saturation capacity at one or both existing upgrading plants could displace up to four of such units. Aromatic saturation of virgin and synthetic crude middle distillates, some hydrocracked middle distillates-especially where synthetic crude oil is processed - and catalytic cracked light cycle oil may all be needed. Thus, a significant Canadian market is foreseen for aromatic saturation units <u>if</u> a diesel aromatic specification becomes fact.

A few units may evolve, in any case, to ease Jet A producer problems due to synthetic crude oils (and other high aromatic crudes in the future).

In the short term, up to three kerosene saturation units are possible and in the long run - 1995 and later - another five diesel oriented saturation units are likely if the aromatic content of diesel fuel is controlled.

1.3 REFINER ALTERNATES

1.3.1 Overview

Prior to an aromatic specification on diesel fuel, refineries using syntnetic crude oil can be assumed to bring the cetane up to specifications by utilization of conventional light crudes and cetane improver chemicals. There will be continuing pressure on synthetic crude oil producers to provide better quality middle distillates since refiners now short of Jet A will tend to more conventional light crudes and consider aromatic saturation as a last resort. Solvent extraction is a proven possibility that may be used in isolated cases (but disposal of the aromatic extract will generally present a major challenge).

It appears likely that new aromatic saturation facilities will be needed somewhere in the system as synthetic crude oil use expands and jet fuel demands increase. They will definitely be needed if a diesel aromatic specification is applied (unless an economic route via extraction can be found).

1.3.2 Aromatic Saturation

In this study, for convenience only, hydrogenation alternates have been grouped into six classes:

Type I - Platinum Sulpnide - The major example is Unocal's Unisar process in which the sulphur in the feed is all converted to H_2S before passing through a platinum catalyst bed. Pressures are modest - below 6.9 MPa, but temperatures are above that needed in other platinum and nickel routes. Some feedstock is hydrocracked to naphtha and light ends but product yield is still in the order of 100 volume percent on feed. The licensor claims the ability to handle feeds containing up to 10,000 ppm (weight) of sulphur and the process is well proven on kerosene boiling range feeds.

Type II - Platinum - In this approach, a low total sulphur feed is essential for today's catalysts, generally below about 15 ppm. One developer indicates up to 150 ppm should be possible in a year or two. This route has long been used for cyclohexane production from benzene and is also in use for solvent production, including one Canadian unit where some kerosene boiling range material may be processed. The Shell Scotford refinery's middle distillate saturation unit is also in this category. ARCO has had a kerosene saturation unit operating for 20 years in the U.S., still using the first charge of platinum on alumina catalyst. Virtually every catalyst vendor has a suitable catalyst, all regenerable; operating conditions are mild - below 200°C and 5 MPa.

Type III - Nickel - Nickel catalysts are currently very competitive with platinum at very low feedstock sulphur levels, say below 2 or 3 ppm. However, they are not regenerable and sulphur accumulates as a poison. Guard beds of special nickel "adsorbents" can be placed before high activity nickel (or platinum) catalysts to reduce the sulphur level to the catalyst appreciably. Operating conditions for nickel catalysts are quite similar to those for platinum. Nickel has also been used in a slurry mode for benzene and, possibly, naphthalene hydrogenation. Generally, nickel catalyst systems are customer designed, but UOP does licence a nickel version of its BH Unibon process for benzene hydrogenation. Copper and cobalt have been added to nickel in two commercially available catalysts to slightly improve sulphur tolerance and reduce the hydrocracking tendencies of pure nickel catalysts.

Type IV - Miscellaneous - This is a "catch all" category, used here to note that there are new catalysts coming into the refinery hydrogenation market. These are often ones that have proved successful in other industries and are being adapted for petroleum product aromatic saturation. Generally these appear to be sulphided catalysts more active than conventional nickel molybdenum catalysts.

Type V - Conventional NiMo and NiW - Operating at moderate temperatures with minimal hydrocracking and minimum equilibrium impacts on aromatic reduction, this route is assumed herein as the conventional route. It has been extensively used outside Canada and the U.S. for kerosene improvement. The required pressures range from 10 to 20 plus MPa and specialty applications - e.g. white oils - can go to the 25 MPa level. This route has significant sulphur and nitrogen tolerance but may require a dual catalyst approach, or special high temperature (CoMo) reactor in the system, for high sulphur content feedstocks (to meet projected middle distillate sulphur specifications). Catalysts in this group are all regenerable and their costs are the lowest of all alternates.

Type VI - Mild Middle Distillate Hydrocracking - Operating at higher temperatures with Type V catalysts, or with specifically formulated catalysts with promoter(s) and a silica alumina base, this route enhances cetane more than the preceding routes due to the production of higher cetane, lighter aromatic and paraffinic compounds from the heavier multi-ring aromatics present in the feed. It does not do as good a job reducing aromatic content, due to equilibrium constraints. Middle distillate yield drops compared to the other routes, to 92 to 94 volume percent, but the difference shows up in a good quality naphtha which is as valuable as the middle distillate product. This route is used by Petro-Canada in Edmonton for synthetic crude oil middle distillate cetane improvement and a similar unit is under construction, as part of the Regina NewGrade Project. Gulf/Chevron and Unocal are the major promoters of this approach, each providing the catalyst to one Canadian unit. Syncrude has a similar unit for selected middle distillates under construction, to be complete in 1988.

Generally, as one follows through from the Type II to Type VI processes, the capital cost increases as the pressures and temperatures rise. However, the

sulphur tolerance also rises markedly. In Canadian middle distillate scenarios the lack of sulphur tolerance of platinum and nickel catalysts will normally necessitate a prior hydrodesulphurizer before the Type II and III processes. Such hydrodesulphurization is not well defined as there has been little demand for ultra low sulphur middle distillate (except for certain solvents).

Currently only certain of the catalysts used in Types V and VI routes are manufactured in Canada. Capability probably exists for at least finishing a Type III nickel catalyst, and full manufacturing capability could be readily added.

1.4 TYPICAL CANADIAN FEEDSTOCKS

The four feedstocks selected for analysis generally cover the range of feedstocks which Canadian refiners may consider:

Suncor Kerosene - This is heavier in a full boiling range than most kerosenes and is a major S.C.O. component similar in middle distillate aromatic content to domestic crudes, but lower in sulphur content at 200 parts per million or less. The aromatic content, 23 to 30 percent, of the jet fuel fraction is generally above the product specification, and the smoke point below standard. The cetane number of the whole fraction is well below 40.

Syncrude Middle Distillate - The largest volume synthetic middle distillate with qualities which necessitate two current major refinery middle distillate improvement units for jet fuel and diesel fractions. This stock is expected to increase in availability by 50 to 70 percent over the next ten years. Here it is assumed that the 1989 version applies (after completion of the current middle distillate hydrotreating unit). The quality may improve about the mid 1990's if added upgrader hydrotreating proceeds as part of a major expansion, but such is not assumed here.

Blend of Virgin Crude: Diesel - 70 Percent and Light Cycle Oil - 30 Percent - If a diesel aromatic specification is imposed, this is expected to be the major aromatic saturation unit feedstock in Canadian refineries.

Light Cycle Oil - This is the poorest feedstock considered with an aromatic content near the 70 percent level. The availability of light cycle oil from catalytic cracking is only about 20 percent of the total middle distillates in an average refinery; hence, a smaller unit is considered than for the other feedstocks.

In the latter two cases, existing low pressure hydrotreating facilities have been assumed available. Additional conventional hydrotreating capacities are expected due to probable reduction in the allowable sulphur content of middle distillates in the early '90's. The facilities will provide bulk desulphurization to the 2000 to 3000 ppm level and olefin saturation at lower costs than if performed in added facilities attached to aromatic saturation units.

The data generated in analyzing alternates for these four feedstocks will provide a base for consideration of variations of the particular feed and of

other feeds of interest in Canadian contexts. As there may be one or two cases where very low sulphur and nitrogen content feedstocks are available, saturation only will be considered assuming the Suncor kerosene data.

1.5 COMPARISON

1.5.1 Preamble

In order to assess the competitive nature of the nickel catalyst route a comparison has been made for each of the four feedstocks with a "conventional" nickel molybdenum (NiMo) route. The nickel route requires prior hydrodesulphurization and hydrodenitrogenation to the 1 ppm level and such facilities were included for the comparison. However, at the end of this section some notes are added relative to costs without prior hydrodesulphurization for very low sulphur feed cases (of which there may be a few).

A target of 20 percent volume percent of aromatics in the final product was assumed in all cases. As the nickel route can achieve a much lower aromatic level, partial feed bypassing has been assumed for the two S.C.O. component cases to minimize costs. The use of bypassing will result in higher concentrations of multi-ring aromatics in the product than with the conventional NiMo route, and this may result in a slightly poorer product for the nickel route at the same total product aromatics level. The other two cases do not permit significant bypassing as the sulphur content must be reduced as well as that of aromatics.

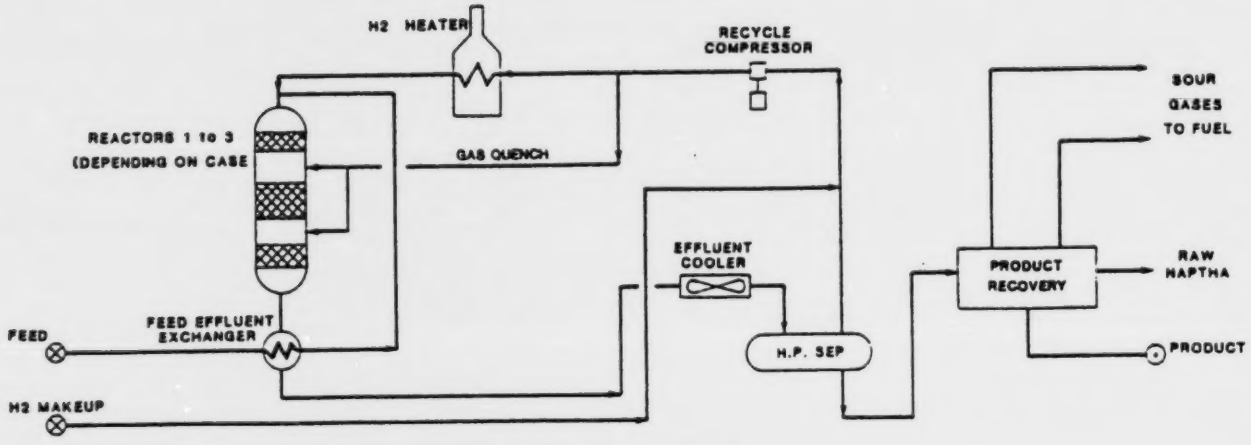
Unit sizes of 2000 m^3/d have been assumed for all feeds except for light cycle oil case, in which case a 1000 m^3/d unit better fits likely scenarios.

1.5.2 Conventional NiMo

Table 1.5.2-1 briefly summarizes the assumed parameters for each case. Figure 1.5.2-1 outlines the basic process scheme assumed. Minor variants will occur from case to case and most heat exchange is not shown.

Table 1.5.2-1
CONVENTIONAL NiMo PARAMETERS

	Suncor Kerosene	Syncrude Middle Distillate	Blend S.R. Diesel and Light Cycle Oil	Light Cycle Oil
LHSV	2.0	1.5	1.0	0.8
Average Reactor Temperature, °C	280	280	315	335
Pressure, MPa	10.1	11.5	13.1	15.2



SIMPLIFIED DIAGRAM OF CONVENTIONAL NiMo SATURATION

FIGURE 1.5.2-1

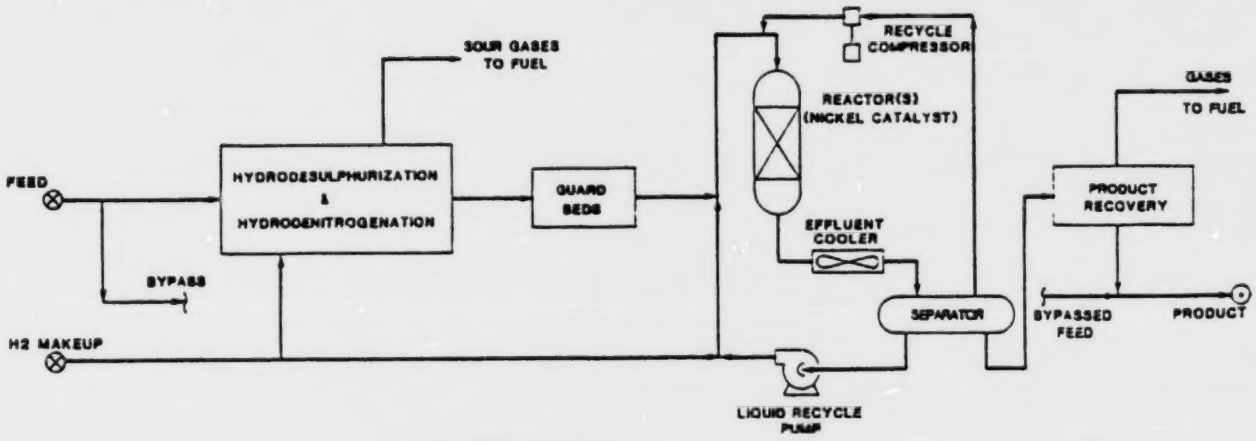
A gas quench system has been assumed to control the temperature to each catalyst bed. The number of reactors and the number of beds vary from case to case, indicative of the high exothermic heat of aromatic saturation, particularly with the light cycle oil.

1.5.3 Nickel

Table 1.5.3-1 briefly summarizes the assumed parameters for each case and Figure 1.5.3-1 outlines the basic process scheme.

Table 1.5.3-1
NICKEL SATURATION PARAMETERS

	Suncor Kerosene	Syncrude Middle Distillate	Blend S.R. Diesel and Light Cycle Oil	Light Cycle Oil
% Treated	40	55	100	100
% Bypassed	60	45	0	0
Desulphurization/Denitrogenation Stage				
LHSV	2.0	1.5	1.2	0.8
Average Reactor Temperature °C	355	361	361	361
Pressure MPa	8.4	10.5	10.5	10.5
Nickel Saturation Stage				
LHSV	4.0	3.0	3.0	1.5
Average Reactor Temperature°C	210	210	210	210
Pressure MPa	3.2	4.2	4.2	4.2



SIMPLIFIED DIAGRAM OF NICKEL SATURATION ROUTE

FIGURE 1.5.3-1

The greater complexity of tne nickel route is immediately obvious. The first stage (hydrodesulphurization/hydrodenitrogenation - HDS/HDN) facility, using CoMo catalyst itself, is very similar to the conventional NiMo route, albeit at somewhat lower pressure and with reduced catalyst inventory.

Nitrogen and water are nickel catalyst poisons at a level of 1 ppm or more; hence, excellent denitrogenation and water stripping are required in the first stage. A sulphur level of 5 ppm has been assumed in the HDS product due to incomplete removal and to recombination of H_2S and traces of olefin (formed at the relatively high temperature needed to obtain the low sulphur level with a CoMo catalyst). Nitrogen removal to below 1 ppm has been assumed.

In order to insure a reasonable catalyst life, a special nickel adsorbent is placed before the reactors to adsorb virtually all the sulphur in the HDS product. The sorbent holds about 10 times the amount of sulphur the catalyst can hold before being deactivated. In practice, some spent catalyst will be used before the special sorbent to reduce adsorbent makeup. On its own the catalyst is not adequate as an adsorbent as it "bleeds" through a portion of the feed sulphur while the adsorbent adsorbs essentially 100 percent prior to breakthrough.

A fixed bed reactor is now foreseen, although there may be some promise in slurry or ebullated bed systems. A liquid recycle approach is used to control the reactor temperature and to remove the heat of reaction. In all cases, except for the Suncor kerosene, multiple reactors are used with the feed split equally and interstage cooling employed to control reactor temperatures. A commercially available high nickel content catalyst has been assumed.

1.5.4 Cost Comparison

Table 1.5.4-1 summarizes the capital and operating costs estimated for each feedstock and the two process routes, assuming current Western Canadian costs. Liquid yields are essentially tne same for the two routes: very slightly less for the nickel route due to the higher temperature of the HDS stage compared to the conventional NiMo reaction, causing more hydrocracking. (No significant

weight loss is foreseen in the nickel saturation system.) Hydrogen demand is slightly higher for the nickel route due to the added nickel stage separation losses

Table 1.5.4-1
COST COMPARISON
- in millions of '87 Canada dollars -

FEEDSTOCK	Suncor Kerosene	Syncrude Middle Distillate	Blend S.R. Diesel and Light Cycle Oil	Light Cycle Oil
RATE(m^3/d)	(2000)	(2000)	(2000)	(1000)
		CAPITAL		
NiMo	20.3	24.0	29.5	29.5
Nickel	21.6	26.5	34.3	32.4
		OPERATING ANNUAL*		
NiMo	1.7	1.8	2.4	2.3
Nickel	2.1	2.7	4.1	3.7

* Exclusive of hydrogen makeup cost

The capital costs of the nickel route are slightly higher in all cases. However, the operating costs of the nickel route are significantly higher than those of the conventional route - due to the nonregenerable catalyst, slightly poorer energy efficiency and greater complexity. Some saving may be achieved with high volume production of nickel catalyst. It is very important to note that approximately 75 percent of the capital cost and 65 percent of the operating cost, exclusive of hydrogen makeup, of the nickel route is for the first stage HDS facility. The nickel saturation stage is inexpensive by comparison (other than for hydrogen supply).

UOP provided a capital estimate for a light cycle oil AH Unibon unit in U.S. Gulf Coast terms. Such a unit would be very similar to the nickel route discussed above, except that the second stage uses platinum instead of nickel. Converting their capital estimate to Canadian conditions and to the 1000 m^3/d size used above indicates a cost within 5 percent of that noted for the nickel route - a remarkably close check given the somewhat differing bases, siting and estimating approaches.

1.5.5 Nickel Without Prior Hydrotreating

The capital cost of a 800 m^3/d unit to reduce aromatics to a very low level without prior hydrodesulphurization and hydronitrogenation, but with expanded guard bed capacity to handle 10 ppm of sulphur in the feed, is estimated at approximately $10,000,000, including catalyst and guard beds. Such a unit will enable 2000 m^3/d of Suncor, or equivalent quality, kerosene to meet a 20 volume percent aromatics specification.

A larger and more elaborate guard bed system is needed in order to minimize adsorbent use through added use of spent catalyst. Such a unit will fit into

cases where kerosene is now hydrotreated along with naphtha and the sulphur is below 10 to 12 ppm, in the kerosene. Hydrocrackers operating on synthetic heavy gas oils will normally achieve this level of sulphur, but some may have nitrogen contents above the assumed maximum allowable of 1 ppm, necessitating prior hydrotreating as no nitrogen compound adsorbent appears now available.

1.6 CONCLUSIONS

The definition of "aromatic" varies greatly from test procedure to test procedure, and author to author. There is a great need for standardization of procedures and of nomenclature.

Figure 1.6-1 provides a very simplified overview of the "fit" of various middle distillate aromatic saturation routes as developed in this study.

This study concludes a route using currently available nickel catalysts will be competitive for aromatic saturation, when the sulphur content of the feedstock is below 5 ppm. In certain circumstances a route will be competitive in the 5 to 15 ppm range (competing with platinum) and over 5000 ppm competing with NiMo and NiW catalysts.

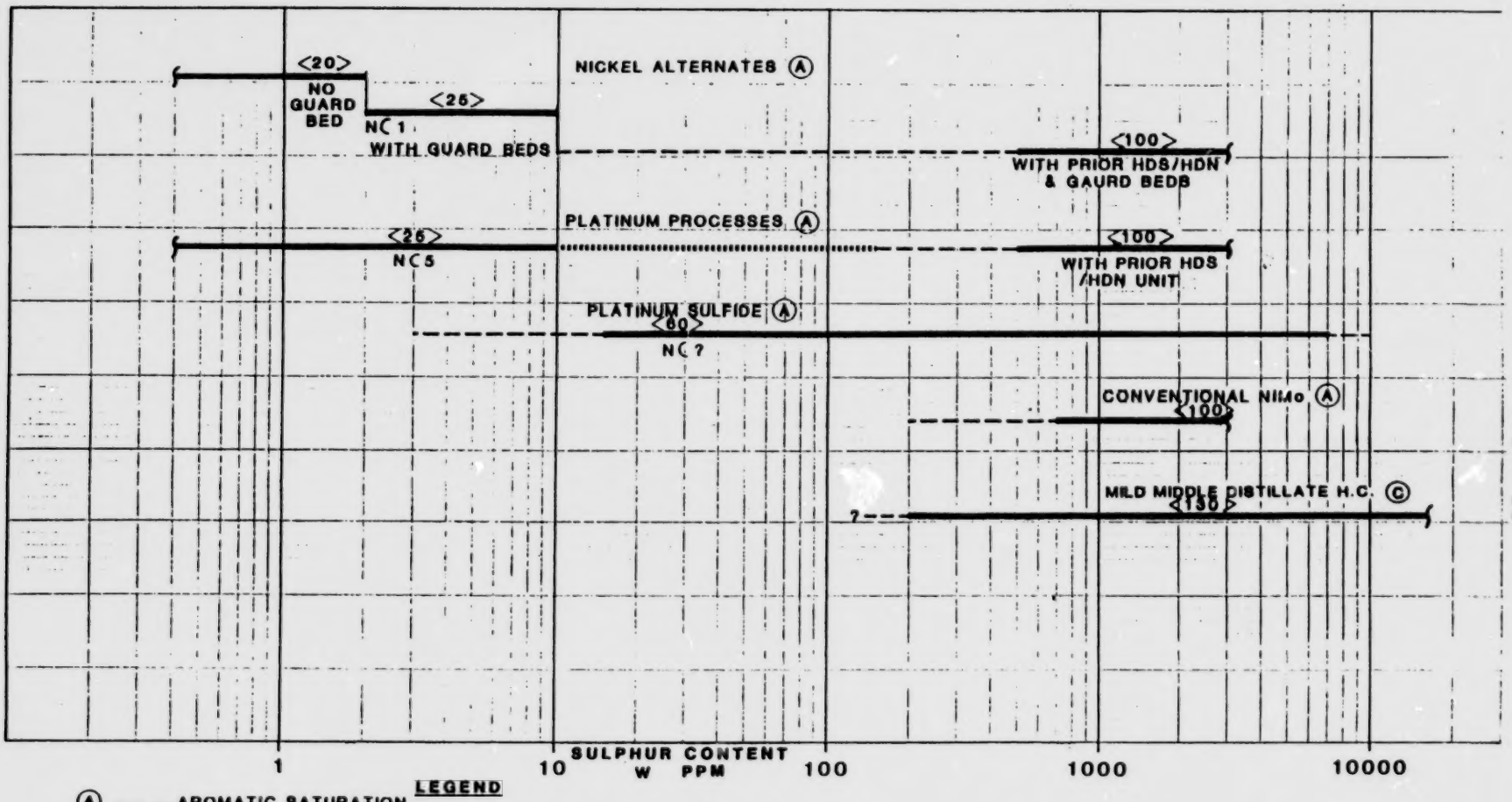
The ability of what is called "Mild Middle Distillate Hydrocracking" to improve cetane beyond that possible through aromatics saturation alone is to be noted. However, Mild Middle Distillate Hydrocracking may not, in all cases, provide enough aromatic saturation to reach jet fuel or future diesel aromatic specifications.

The platinum sulphide route may not economically achieve the very low aromatics levels possible with the other platinum and nickel routes such as may be required for solvents. However, ultra low levels are not necessary for jet and diesel fuels and the small increase in unit throughput - i.e. less bypass- will not unduly hurt economics with feedstock up to its sulphur tolerance limit.

The major role sulphur tolerance plays in the selection of an aromatics saturation process is to be noted. Catalyst cost relationships are not so obvious, but the non regenerability of current nickel catalysts certainly offsets much of the lower initial catalyst cost compared to platinum based routes.

1.7 RECOMMENDATIONS

In further development of a nickel based route, attention should be directed to the current lack of sulphur and nitrogen tolerance. A regenerable nickel based catalyst would be highly desirable. There is also a need to investigate optimum hydrodesulphurization conditions and catalysts, to see if the very high capital cost of that portion of the unit can be reduced. In the short term the emphasis should be on Jet A production.



APPROXIMATE ECONOMIC FITS
MIDDLE DISTILLATE
SATURATION PROCESSES

FIGURE 1.6-1

CANMET should assist the industry in bringing about standardized test and reporting procedures covering all forms of aromatic compounds in middle distillates. Correlations between aromatics and combustion properties of both jet fuel and diesel fuel warrant further work in order to optimize middle distillate aromatic saturation and jet and diesel fuel quality improvement in general.

Extraction may prove applicable for certain jet fuel improvement situations and some work appears warranted in that regard.

2. INTRODUCTION

2.1 TERMS OF REFERENCE

By contract dated June 16, 1987, the Federal Department of Supply and Services (DSS) retained RTM Engineering Ltd. to undertake an "Assessment for the Potential for Commercialization of a Low Severity Catalytic Hydrogenation Process for Middle Distillate Upgrading" for the Department of Energy Mines and Resources (EMR). This report summarizes that assessment.

Two interim reports were written to update CANMET (Energy Research Laboratory of EMR) staff relative to task number two, literature review, and to task number three in which two process routes were compared. An informal presentation of the second interim report was made to staff on September 18, 1987 in Ottawa and a final presentation was made on November 3, 1987.

Mr. M. Skubnik has been the Scientific Authority for EMR on this project, with Dr. M.F. Wilson also interfacing closely. Ms. Gaetane Degenais was the Science Procurement Officer for DSS.

This study has been undertaken to compare the economics of low pressure nickel catalyst route for middle distillate aromatic upgrading being investigated by CANMET with a "conventional" nickel molybdenum route and to develop an understanding for the potential Canadian markets for such a process. The CANMET investigations into nickel have been part of an ongoing program to develop better processes to improve the relatively low quality of the middle distillate portion of Canadian synthetic crude oils.

2.2 METHODOLOGY

This study has been laid out in five tasks as follows:

Task #1 Data Compilation: At the outset, EMR provided a detailed review of their work to date (87)(111)(114)(115). In this task, open literature and catalyst developer and manufacturer literature were reviewed and a large number of contacts made with refining and upgrading companies. (In practice, the literature search continued through the study with excellent input from the CANMET team.)

Task #2 Selection of Options: For each four feedstocks, conventional hydrosaturation was compared with the low pressure route (and comparison hydrodesulphurization). In each of the eight cases, major equipment were sized from preliminary process calculations and then estimated. Factors were used to convert to overall facility capital costs. Operating costs were then estimated.

At this time an analysis was made of the future Canadian refining settings and of the potential for new process route.

Task #3 Interim Report: This report covered the results of Task #2, showing costs as well as process market potential.

The Task #3 report was presented at a September 18, 1987, Ottawa meeting.

Task #4 Consultations: Discussions with selected refiners and upgraders and a catalyst vendor relative to the study, potential markets foreseen for the process and areas of recommended future work.

Task #5 Final Report: As presented here with a verbal presentation and discussion on November 3, 1987.

The RTM team has been organized as follows:

T.J. McCann	Study Manager and Principal Consultant
R.G. Abbott°	Overview and Process Advice
H. Marshall°	General overview
M.A. Schoening	Environmental Issues
K.W. Padgett* and G. Denis*	Conventional Hydrotreating Process Balances and Sizing
R. Towell	Vessels and Exchanger Estimating and Cost Factors Generally
T. S. Royan	Air Cooler Estimating
J. Harbert	Compressor and Pump Estimating
N. Tatz	Literature Search and General Assistance

° Calgary Synfuels Staff * Padgett Process Services Ltd. Staff

Other RTM staff have assisted in both technical and administrative aspects.

2.3 "AROMATICS"

The definition of aromatics varies from author to author, and test procedure to test procedure. Nomenclature used relative to individual types of aromatic compounds also varies from reference to reference. One recent paper provided correlations against two aromatic content test methods to illustrate the confusion that exists (121).

At this time, of the high sales volume petroleum products, only Jet A has an aromatic content specification - total aromatics and naphthalenes. For jet fuels, the test procedures used are reproducible and generally acceptable. However, it is to be noted that naphthalenes are seldom of concern and that the total aromatics specification has been relaxed somewhat in recent years. The

combustion property specifications - e.g. smoke point - appear more rigid and of greater importance in the end use in any case.

Herein, the convention established in jet fuel testing of indicating total aromatics on a volume percentage basis is generally followed. Unless otherwise noted, the word aromatics refers to total aromatics and when concentration is shown, it is on a volume basis. Where aromatic compounds have more than one aromatic ring, generally they are referred to as polynuclear aromatics - PNA's - in accordance with current oil refining literature. However, where possible, specific compound types are noted.

While C_{13} NMR measurement of hydrocarbon types is definitely preferred, and available in some references, this report has not attempted to "correct" any literature data to a common analytical base. Often the original reference nomenclature is also used, as a precise definition of its meaning is not available.

CANMET have already started work on a new aromatics test procedure (35).

2.4 ACKNOWLEDGEMENTS

Tne CANMET team provided very appreciable input in the form of test data, literature references and comments. RTM thanks go to Mr. Skubnik and Dr. Wilson for their full cooperation.

Personnel with Suncor, Syncrude and Esso Petroleum Canada provided advice on markets, processing and kinetics. Virtually all catalyst developers and manufacturers have provided input relative to process routes and catalysts of today and possibly tomorrow as noted in the Bibliography and Personal Communications section at the end of the report.

3. PROCESS MARKET ASSESSMENT

3.1 PREAMBLE

National Energy Board (1986) forecasts have been used relative to product demands and crude types to provide background on refining in the future (69). However, the ultimate potential for an aromatic saturation process will only be known if/when new specifications for Canadian middle distillate products are defined.

The following regions were selected for use in this analysis, as having refineries serving generally equivalent market areas and processing similar crudes and as having National Energy Board and/or Statistics Canada data available as a group:

- Atlantic - Encompassing three refineries at St. John, N.B. and Halifax, N.S.
- Quebec - Encompassing three refineries at Montreal and Quebec City.
- Ontario - With six refineries in Mississauga, Oakville, Nanticoke and Sarnia areas.
- West - With 11 significant refineries in Regina, Calgary, Edmonton, Fort Saskatchewan, Taylor, Prince George and Vancouver and two oil sand upgrading facilities in northern Alberta.

Montreal is assumed supplied from offshore (or east coast) sources as the throughput of the Interprovincial Pipeline Limited (IPL) from Sarnia to Montreal is currently low and the NEB projects no flows east in 1995.

The following refineries have been neglected in this analysis:

- Come by Chance - Newfoundland Processing considered strictly export oriented with imported crude.
- Moose Jaw - Petro-Canada, asphalt only
- Lloydminster - Husky, asphalt only
- Bowden, Alberta - Shell (Parkland later in year) mini-condensate feed, gasoline oriented.
- Vancouver - Shell, partially semi refined feedstock
- Vancouver - Petro-Canada, largely semi refined feedstock in future
- Norman Wells - Esso, mini topping refinery.

Kemtek in Montreal has been neglected due to its petrochemical orientation.[1]

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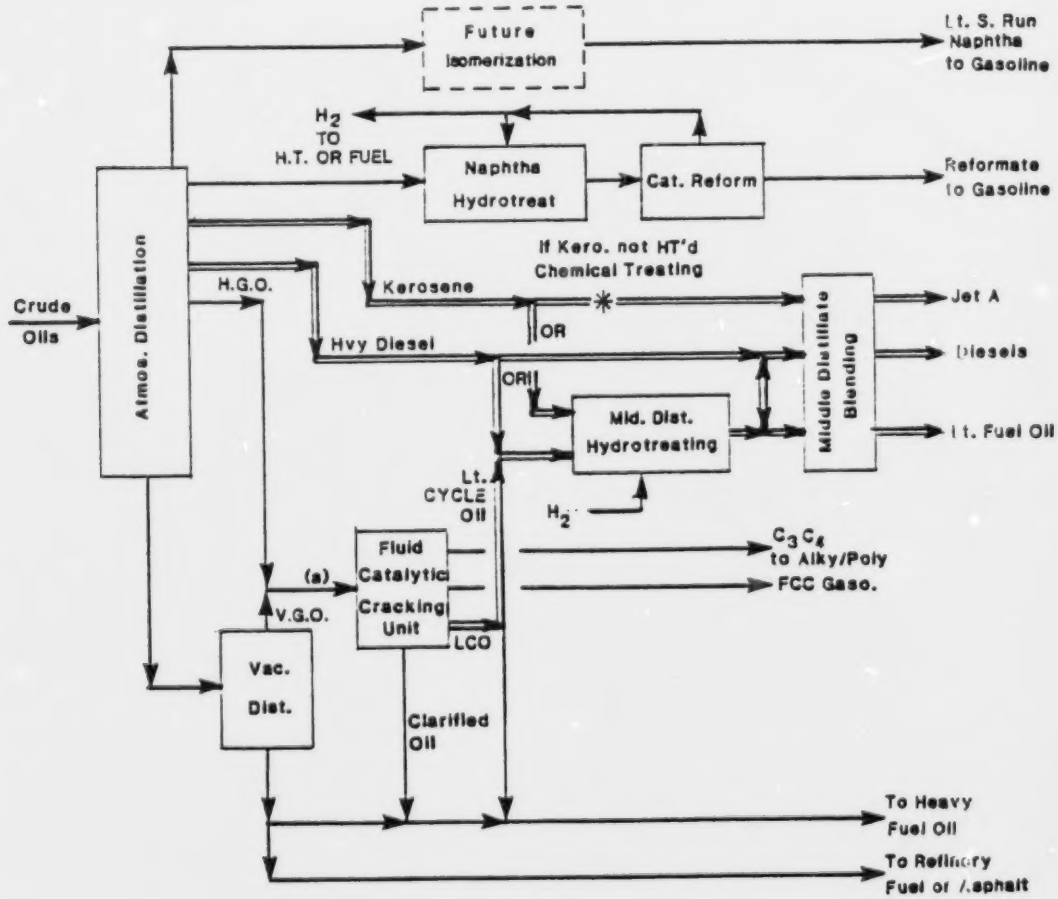
[1]Kemtek's shutdown benzene hydrogenation unit could be used for hydrogenation of middle distillates with very low sulphur content. Either platinum, as in the past, or nickel catalyst could be used. This unit could well form a test unit for the CANMET route, if suitable offsite hydrodesulphurization can be obtained.

Pyrolysis middle distillates enter the middle distillate pool from both Petromont and Polysar but the quantity is small and neglected herein. Institut Francais du Pétrole (IFP) notes an ability to upgrade such distillates to jet fuel through very deep hydrotreating; hence, they should not be disregarded in further studies (34).

3.2 EXISTING REFINERIES

Figure 3.2-1 outlines a typical conventional Canadian refinery configuration and notes which intermediates go into the middle distillate pool:



NOTE: (a) HYDROCRACKERS OPERATE ON SELECTED GAS OIL STREAMS IN 6 REFINERIES IN PARALLEL WITH CATALYTIC CRACKING

SIMPLIFIED OUTLINE OF TYPICAL CANADIAN REFINERY

FIG. 3.2-1

Virgin Kerosene and Diesel fractions with or without hydrotreating. Any unhydrotreated kerosenes and some light diesels usually receive a mild chemical treatment to convert mercaptans to disulfides with less odour and more stability.

FCC light cycle oil - normally hydrotreated for stability and sulphur content.

Where hydrocrackers are present, their middle distillate products also enter the middle distillate pool. Hydrocrackers processing synthetic crude and similar aromatic fractions often do not produce specification Jet A grade kerosene, the aromatic content is too high and smoke point may be poor. Table 3.2-1 provides selected Canadian refinery statistics based on Oilweek and Oil and Gas Journal surveys with some corrections by RTM (74)(79). At three refineries coker processing of residuals also produces middle distillate components, as does the CANMET residual hydrocracker at the Petro-Canada Montreal refinery.

While hydrocrackers can be operated to maximize the yield of middle distillates, the majority of Canadian units are operated to produce naphtha from heavy gas oils. Much of the naphtha is used at Petro-Canada Montreal, Shell Sarnia, Esso Sarnia, Suncor Sarnia and Shell Scotford to produce benzene and other petrochemicals as well as gasoline. However, recently an Irving representative noted that their hydrocracker was producing about 40 percent middle distillates in a low severity operation with the unconverted gas oils going to their fluid catalytic cracking unit (FCCU), presumably in line with low gasoline demands in the Maritimes (75).

Shell Scotford currently operates and Consumer's Co-operative will, by late 1988, operate refineries with all S.C.O. feedstocks. At Co-op, the refinery and NewGrade heavy oil upgrader will operate integrally. Otherwise, only Petro-Canada in Edmonton and Suncor in Sarnia have extensive process capabilities for S.C.O.'s. Petro-Canada can take up to 35 percent of total charge and Suncor up to about 90 percent. Chevron, in Burnaby, has a small fractionator for S.C.O.'s in parallel with their main crude unit.

Shell Scotford and Petro-Canada Edmonton have middle distillate process facilities to produce reasonable cetane diesels and specification jet fuels from synthetic crude oils. Shell uses a platinum catalyst based saturation unit processing a portion of their middle distillates (85). Petro-Canada has what is called herein a "mild middle distillate hydrocracking" operation (in blocked mode with conventional gas oil hydrocracking) (10). The Consumer's Co-operative/NewGrade heavy crude oil/refining complex will have a very similar system to that at Petro-Canada when it is fully on stream. At Regina there will be an ability to produce up to a 45 cetane diesel from a blend of virgin heavy crude, coker, residual hydrotreating and hydrocracker middle distillate after the NewGrade units are complete.

The Shell and Esso Sarnia area refineries contain small aromatic saturation units for solvents, part of whose feed boils in the kerosene range. Other existing middle distillate hydrogeneration capacity is all lower severity operation to reduce jet fuel, diesel and light fuel oil sulphur to current sulphur specifications.

TABLE 3.2-1
SELECTED CANADIAN REFINERY DATA
UNIT CAPACITIES
m^3/cd

Region	Company	Location	Crude	Thermal	Catalytic Cracking	Hydrocrack	Mid Dist. Hydrotreat	Hydrogen Units(C)	Other
Atlantic	Esso	Dartmouth, N.S.	13.1	-	1.9	-	5.3(B)	-	-
	Irving	St. John, N.B.	20.0(A)	2.9VB	2.7	2.8	6.3(B)	1.13	-
	Texaco	Dartmouth, N.S.	3.2	-	1.0	-	0.8	-	-
Quebec	Petro-Canada	Montreal	13.9	2.0VB	2.3R	2.3	1.4	1.27	Aromatics 0.5 CANMET Resid HC
	Shell	Montreal	19.1	1.9VB	3.4(D)	1.7	6.7	0.42	Lubes
	Ultramar	St. Romauld	16.4	-	3.9	-	1.7	-	-
Ontario	Esso	Sarnia	19.6	3.0FC	3.6	1.8	6.0(B)	-	-
	Petro-Canada	Clarkson	9.5	-	S/D	1.7(E)	1.3	0.38	Lubes
	Petro-Canada	Oakville	12.8	-	4.2(B)	-	1.2	-	-
	Shell	Sarnia	11.3	0.5VB	2.4	1.1	1.4(B)	-	Aromatics
	Suncor	Sarnia	11.1	0.8VB	2.4T	2.9	0.6	1.08	Aromatics
	Texaco	Nanticoke	15.1	-	5.8	-	-	-	-
Sask.	Cons. Co-op (Before NewGrade)	Regina	7.7	1.1DC	2.2	-	0.5	-	-
Alberta	Esso	Edmonton	26.2	-	7.2	-	4.5	-	Lubes
	Petro-Canada	Edmonton	19.3	1.2DC	5.7	3.0(F)	7.3(G)	0.87	-
	Shell	Ft. Saskatchewan	8.9	-	-	5.1	2.8	1.42	Aromatics
	Turbo	Calgary	4.4	-	1.4	-	1.1	-	-
British Columbia	Chevron	Burnaby	5.7	-	1.4	-	-	-	-
	Esso	Ioco	6.8	-	1.8	-	1.8(B)	-	-
	Husky	Prince George	1.5	-	0.4	-	0.8(G)	-	-
	Petro-Canada	Port Moody	5.9	-	S/D(H)	-	2.2	-	-
	Petro-Canada	Taylor	2.8	-	0.3	-	1.1	-	-
	Shell	Burnaby	3.8	-	1.0	-	1.6	-	-

LEGEND

Thermal - VB - visbreacker, FC - Fluid Coker, DC - Delayed Coker

Catalytic Cracking - T - Houdriflow moving bed - all other units are fluid catalytic crackers (FCC)
R - FCC can process significant vacuum bottoms from light low metals crudes

Aromatics - Benzene and other aromatics produced

Lubes - Part of Heavy Gas Oil to lubricating oil

Notes:

A) Arbitrarily derated to conventional refinery configuration by deletion of part of crude capacity
B) Two or more units.
C) Feed natural gas in most cases except Irving. Units are million m^3/d
D) New residual feed FCC in construction.
E) Lube oil oriented.
F) Continued deep middle distillate hydrotreater and heavy gas oil hydrocracker for synthetic crude oil fractions.
G) Part of capacity combined with naphtha processing.

3.3 CRUDE OILS

3.3.1 General

Canadian refineries, with a few exceptions, run light and medium crudes except for asphalt production. The lighter crudes fit Canada's gasoline and middle distillate oriented markets.

Table 3.3.1-1 presents selected data on types of crude which are being (or have been) run in Canada (74). The particular crudes were selected to match imports to Atlantic and Quebec refineries, in 1986 and 1985 from Iran, Mexico, Nigeria, Venezuela and the North Sea. In '85, Algerian crude was much used as were Saudi Arabian crudes in '86 (in Atlantic region only). The mix of imported crudes varies greatly year-to-year and refinery to refinery: generalities are not possible. The table is intended to indicate that:

a) There are wide varieties of composition even at the same gravity (21).

b) The aromatic content of most kerosenes and virtually all virgin diesel fractions is above 20 percent. In practice, a lower end point on the kerosene than that used in the table, will result in meeting a 22 percent Jet A aromatics specification - with allowable variance to 25 percent - in most cases without aromatic saturation.

c) Most virgin diesel fractions are above 0.1 percent by weight in sulphur content - Syncrude and Suncor middle distillate fractions and Beaufort Sea crude being notable exceptions.

d) Many conventional kerosene fractions are also above 0.1 percent in sulphur content. Only a few kerosene cuts are under 0.05 weight percent in sulphur content.

Crude blends generally tend to become heavier and higher in sulphur with time. For example, the IPL blends moving east have seen heavier and higher sulphur crudes replace declining premium light crudes. As the crudes making up a blend change with time, the fractional yields and characteristics change - e.g. Beaufort crude would not greatly affect light crude blend gravity but would have a major impact on the middle distillate yield.

The IPL system also creates significant interfaces due to the length of the line and inherent intermingling and tankage operations, especially at Superior, Wisconsin. At Sarnia, 3 to 10 percent contamination can be expected. This contamination increased appreciably at Montreal due to the slow rate east of Sarnia and the now daily shutdowns. As IPL have 3 lines to Superior and 2 systems from there to Sarnia, they can generally keep heavy crudes away from very light crudes such as synthetic crude oils and pentanes plus but emergency situations do occur. Buffers are used in some instances to separate different crudes but the buffer stock must go to one or the other of the receiving refineries.

TABLE 3.3.1-1
SELECTED CRUDE ASSAY DATA

		CRUDE °API	CRUDE S	MID DISTILLATE YIELD ON CRUDE Vol% 190-343°C	KEROSENE SMOKE POINT/ AROMATICS/SULPHUR	HVY. DIESEL CETANE/SULPHUR
CANADIAN						
	FEDERATED	39.7	0.2	32	(22)/23/0.07	55/0.2
	RAINBOW	40.7	0.5	24.5	20/24/0.1	59/0.4
	RANGELAND	39.5	0.8	24	20/24/0.2	51/0.5
	GULF ALBERTA	35.1	1.0	23	19/28/0.3	52/0.9
	BOW RIVER	26.7	2.1	24	17?/24/0.4	46/0.1
	SYNCRUDE ('85)	32	0.1	47	15?/36/0.01	(31)/0.06
	BEAUFORT	35	0.15	44	16-18/24/0.03	45/0.09
	HIBERNIA/ TERRANOVA	34?	1?	27?	?	?
MEXICAN						
	ISTHMUS	32.8	0.3	30	22/22/0.2	(55).5/1.2
	MAYA	22.0	3.3	30	20/21/1.2	51/2.2
VENEZUELA						
	LAGOMEDIO	31.5	1.2	25	24.5/20/0.03	50/0.2
ALGERIA						
	ZARZAITINE	43.0	0.07	32	25/14/.02	?/.05
NIGERIA						
	BONNY LIGHT	36.7	0.1	45	21/17/0.2	(49)/0.1
	FORCADOS	29.7	0.3	44	?	(39)/0.2
	BONNY MEDIUM	25.2	0.2	47	19/17/0.04	(38)/0.2
SAUDI ARABIA						
	ARAB LT.	33.4	1.8	29	23/21/0.08	?/1.0
	ARAB HVY.	27.9	2.9	23	26/19/0.2	?/1.3
IRAN						
	LIGHT	33.8	1.35	26	24/18/0.2	?/1.01
	HEAVY	31.0	1.65	24	23/18/0.3	?/1.2
NORTH SEA						
	BRENT BLEND	38.0	0.4	31	26/18/0.04	(54)/0.2
	BERYL	36.5	0.4	32	?/21/0.02	(51)/0.2

NOTES

i. Based on Oil and Gas Journal 1983-13 part series (74). Except for synthetic and frontier, those by RTM.
ii. Most "crudes" are blends which tend to decline with time as poorer individual crudes increase as a precentage in later years.
iii. These are only representative crudes and not necessarily typical of specific crudes processed in Canada.
iv. The kerosene data were taken directly from the sources without corrections for boiling range.

Legend

( ) Estimated ? Gap unknown (where data shown, assumption for this study)

Sulphur is shown in weight percent and aromatics in volume percent

The serious nature of contamination can be seen by using as an example, Bow River 26° API crude contaminating an S.C.O. In this case 5 percent contamination will double the amount of sulphur in the final S.C.O.. The final S.C.O. will now also contain an asphaltene rich vacuum residue of about 2 percent volume compared to none in the original S.C.O., with 6 ppm of nickel and 12 ppm of vanadium now present compared to less than 1 ppm in total before contamination. Conventional FCC units will not be able to handle the 350°C plus material and vacuum distillation will be essential to eliminate the residual material, a step not now necessary in the Edmonton area with S.C.O.

While certain synthetic crude properties swing over a much wider percentage range than do those of conventional crudes from a given field, refining units must be designed for significant variation even with conventional crudes. Sulphur and nitrogen in particular must be carefully noted.

Virtually all conventional crudes exhibit the following middle distillate properties as the boiling point rises - increasing cetane numbers, increasing sulphur and nitrogen contents and decreasing smoke points. Aromatic contents tend to rise with boiling point. The same property trends are exhibited by light cycle oil and S.C.O. fractions that come from the same hydrotreater. But S.C.O. fractions processed under different conditions can produce opposite ends in the overall S.C.O. As pour point also rises with boiling point, all these trends are very important in Canadian middle distillate blending to meet seasonal demands.

3.3.2 Canadian Crude Type Forecasts

The 1986 NEB forecasts for various crude types are shown in Table 3.3.2-1 for both low and high price scenarios (69). Current price trends appear to be nearer the high than the low price case, and generally this discussion follows the "high price" data. Table 3.3.2-2 provides the NEB's frontier crude penetration forecasts for the high price scenario.

Tables 3.3.2-3 and 3.3.2-4 provide an analysis of the penetration of S.C.O. capacity into refineries which do not, or will not shortly, have special S.C.O. processing facilities - assuming no S.C.O. exports or movement to Quebec. Conventional refineries can normally handle between 5 and 10 percent of S.C.O before jet fuel aromatics and/or diesel fuel cetane specification cannot be met. The NEB low price case causes little concern but the high price scenario with greatly increased S.C.O. production indicates major changes in middle distillate processing will be needed (unless exports of S.C.O. alleviate the problem). The recent paper by Devai et al gives an excellent review of the Canadian refiner's concerns with synthetic crude oils (29). Cliffe and Steere discussed the same subject at earlier dates (16)(90)(92)(93).

The very high middle distillate yield of S.C.O. may create problems in the gasoline (G)/middle distillate (D) production ratio unless hydrocracking of middle distillates is practised. High middle distillate yielding conventional crudes such as those from Nigeria and the Beaufort also produce low G/D ratios. Table 3.3.2-4 is briefly illustrating the projected impact of frontier area crudes in the NEB high price scenario.

TABLE 3.3.2-1
REFINERY CRUDE FEEDSTOCK SOURCING*
$10^3 m^3$/day

REGION	NEB CRUDE PRICE SCENARIO	SOURCE	YEAR 1985	1990	1995	2000	2005
ATLANTIC	LOW	DOMESTIC HVY.	0.2	0	0	0	0
		LT. & MED.	2.3	0	0	0	0
		IMPORT	21.2	26.0	26.0	27.0	28.0
	HIGH	DOMESTIC HVY.	0.2	0	0	0	0
		LT. & MED.	2.3	0	3.5	17.5	17.5
		IMPORT	21.2	25.4	20.2	7.1	7.8
QUEBEC	LOW	DOMESTIC HVY.	1.7	2.0	0	0	0
		LT. & MED.	21.7	18.6	0	0	0
		IMPORT	21.3	22.6	45.5	45.5	45.5
	HIGH	DOMESTIC HVY.	1.7	2.0	0	0	0
		LT. & MED.	21.7	17.7	0	0	0
		IMPORT	21.3	22.6	44.5	44.5	44.5
ONTARIO	LOW	DOMESTIC HVY.	8.6	9.7	10.2	10.7	11.3
		LT. & MED.	68.1	73.4	51.1	25.6	28.8
		IMPORT	0.4	0	21.8	46.7	68.9
	HIGH	DOMESTIC HVY.	8.6	9.7	10.2	10.7	11.3
		LT. & MED.	68.1	72.3	61.8	62.8	38.2
		IMPORT	0.4	0	9.1	7.5	31.5
WEST	LOW	DOMESTIC HVY.	4.7	5.8	6.3	7.0	7.7
		LT. & MED.	71.1	70.0	71.5	74.7	78.2
		IMPORT	0	0	0	0	0
	HIGH	DOMESTIC HVY.	4.7	5.8	6.3	7.0	7.7
		LT. & MED.	171.1	68.5	67.5	69.5	72.5
		IMPORT	0	0	0	0	0

Note: * Based on National Energy Board 1986 forecasts (69).

TABLE 3.3.2-2
NEW FRONTIER CRUDE PENETRATION IN CONVENTIONAL REFINERIES*
$10^3 m^3$/day

	Western Frontier NWT	Beaufort	Total	Penetration into Conventional Ontario & West Refining %	East Offshore	Penetration into Conventional Atlantic Refining %
1985	2.9	0	2.9	2.4	0	0
1990	4.2	0	4.2	3.6	0	0
1995	4.2	0	4.2	3.5	3.5	13.5
2000	3.5	17.5	21.0	17.5	17.5	67
2005	2.1	17.5	19.6	15.8	17.5	67

Notes:

* Based on reference (69).

TABLE 3.3.2-3
CRUDE OIL TYPE FORECAST FOR ONTARIO, PRAIRIES AND B.C.
$10^3 m^3$/day

Year	Total Crude Demand				Heavy Crude Demand				Net S.C.O. & Light & Medium Demand	S.C.O. from oil sands & Upgraders	S.C.O. % of Total
	(A) LOW PRICE SCENARIO										
	Ont.	Prairie	B.C.	Total	Ont.	Prairie	B.C.	Total			
1985	78	53	22	153	9	5	9	14	139	26	19
1990	83	54	22	159	10	6	0	16	143	36	25
1995	83	56	22	161	10	6	0	16	145	37	26
2000	83	59	22	164	11	7	0	18	146	37	25
2005	83	64	22	169	11	8	0	19	150	37	25
	(B) HIGH PRICE SCENARIO										
1985	78	53	22	153	9	5	0	14	139	26	19
1990	82	51	23	156	10	6	0	16	140	36	26
1995	81	52	22	155	10	6	0	16	139	44	32
2000	81	54	22	157	11	7	0	18	139	56	40
2005	81	58	22	161	11	8	0	19	142	56	39

Note: i. No S.C.O. movement to Quebec, Maritimes, U.S. or Offshore allowed.
ii. Yukon and N.W.T. demands included in Prairie and B.C. figures, respectively.
iii. Suncor upgrader direct sales to petroleum products market not included.

TABLE 3.3.2-4
S.C.O. PENETRATION
$10^3 m^3$/DAY

Year	(1) S.C.O.+ Upgraded + Light + Medium Demand(c)	(2) S.C.O. Oriented Refinery Capacity (a)(b)	(3) Net Conventional Crude Demand (1) - (2)	(4) Projected S.C.O. Production(c)	(5) Excess S.C.O. (4)-(2)	(6) Conventional Refinery Use of S.C.O. % (5)/(3)x100
			LOW PRICE SCENARIO			
1985	139	23	116	26	3	3
1990	143	30	113	36	6	5
1995	145	30	115	37	7	6
2000	146	30	116	37	7	6
2005	150	30	120	37	7	6
			HIGH PRICE SCENARIO			
1985	130	23	116	26	3	3
1990	140	30	110	36	6	5
1995	139	30	109	44(b)	14	13
2000	139	30	109	56(b)	26	24
2005	142	30	112	56(b)	26	23

Notes:
(a) Includes Shell Scotford 8,000 m3/d
Petro-Canada Edmonton nominal 7,000 m3/d
Suncor, Sarnia nominal 8,000 m3/d
Co-op/NewGrade nominal 7,000 m3/d (1989)
(b) Assumes all S.C.O. and upgraded crudes used in Ontario and Western Provinces.
(c) From Table 3.3.2-3

At NewGrade, only S.C.O. components surplus to Co-op needs will be sold and the middle distillate fraction of S.C.O. sales can be tailored to at least virgin crude quality. Husky proposes a 40 cetane diesel fraction and a Jet A fraction meeting Canadian Government Standards Board (CGSB) specifications.

If the east coast offshore crude quality is reasonably good, e.g. Arabian light or better, Atlantic crudes would change little assuming the NEB's high price forecast. Quebec will still be import crude oriented and will probably tend to lighter crudes given two new residual feed FCC units (not operable on heavy residuals) and relatively low residual fuel oil demands. Ontario will continue with predominantly light crudes but imports could become very important by the late 1990's. Western Canada will continue to be light crude oriented with a high penetration of synthetic crudes. Arctic crudes could push up the virgin middle distillate yields appreciably.

3.3.3 Impacts of Syncrude Type Synthetic Crude Oils

The S.C.O. based refinery will have a normal G/D range of 0.75 to 0.9 and the conventional crude refinery 1.2 to 2.8. Hydrogen balances also will play major roles in the economics of hydrogen required for middle distillate aromatic saturation (29)(30)(85). If aromatic saturation to the 20 volume percent level is needed in all middle distillates, a synthetic crude oil refinery would require roughly 500 m^3 of hydrogen generation per m^3 of S.C.O., whereas a conventional light crude operation would need only about 125 m^3/m^3.

In practice, the conventional refinery will be putting some light cycle oil to railway diesel and/or light fuel oil (in Ontario) and thus come close to balancing hydrogen needs. Very significantly, more hydrogen production will be needed for S.C.O. processing.

When hydrocracking is practiced in all but one current example, steam methane (or other light hydrocarbon) reforming is now used with conventional crude to provide sufficient hydrogen.

More steam methane reforming will be needed in a hydrocracker equipped refinery when S.C.O. becomes the dominant feedstock. Hydrogen yields in catalytic reforming with S.C.O. are less due to the nature of S.C.O. naphtha and its relatively low yield.

3.4 SPECIFICATION CHANGES

About the only thing now clear relative to future middle distillate specifications in the U.S. and Canada, is that the U.S. has promulgated diesel emission standards to take effect for 1989, 1991 and 1994 model years and Canada introduces a new standard on Dec 1, 1988, essentially the same as that which the U.S.adopts, a year later (11)(54)(98). Canada is adopting a wait and see attitude relative to the later U.S. emission standards. There is general agreement that Canada will closely follow the U.S. in the long run as most Canadian diesel engines are designed and built in the U.S. As these standards are relative only to new diesel engines, their impact will build up with time.

It now appears likely that reductions will be made in most Canadian middle distillate sulphur specifications by 1991 with a possible further decline in 1995. The reductions will be both acid rain and diesel engine emission oriented. These charges may be accompanied at that time by tight aromatic standards in diesel if the 1991 changes do not adequately control particulates in diesel engine exhausts.

U.S. EPA suggestions that diesel sulphur should drop to 0.05 weight percent, as in the Los Angeles area, may be setting the long term sulphur specification for diesel regardless of whether economics and environmental needs concur (61)(62)(78)(79)(121). A parallel U.S. proposal for a 20 percent aromatics content in diesel has been largely discounted by many oil industry people at this time, but this study noted several instances where significant "players" are assuming that that will be a future specification.

There are now major research programs underway in the U.S. and Canada to adequately define the relationships of sulphur, aromatics, end point and other variables to gas turbine and diesel emissions and diesel engine trap operation (4)(39)(52)(90). Results of suitable scientific quality for any specification change will not be available until the end of 1988 at best. Prior work is discussed in (typical) references in the footnote but, generally, results to date have not been adequately definitive.[2]

Off road diesel fuel demands are very significant, at least in western Canada-mines, forestry, oil drilling, etc. - and like railway and marine diesels, off road diesel fuel standards are now a matter only between the buyer and seller. In practice, most off road diesel comes from the same tank as road diesel, but that is not essential. The railways now use large quantities of diesel of a cetane quality below that sold for road transport use (48).

It seems reasonable to expect that acid rain concerns will lower jet fuel and light fuel oil, as well as off road diesel fuel, sulphur specifications to the same or nearly the same level as road diesels. Political pressure may result in differing levels between products.

While a variety of scenarios of differing probabilities could be considered, especially with the obscure situation prevailing at this time, it was felt that such an approach would be too complex for this study. The following table provides a simple forecast of possible changes in middle distillate quality standards:

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[2]Typical prior tests on combustion of various diesel and jet fuels are reported in the following: (32)(36)(38)(40)(42)(53)(54)(59)(60)(62)(67)(68)(71)(95)(103)(104)(105)(106)(107)(124).

TABLE 3.4-1
PRELIMINARY ESTIMATE OF CANADIAN
MIDDLE DISTILLATE SPECIFICATION CHANGES

Product	Type	Specification (Maximum)	YEAR 1987	1992	1996	Note
Diesel Fuel	(Road)	Sulphur	0.5*	0.15	0.05	Summer "B" Grade (Reference 12)*
		Aromatics	--	--	25(f)	
		90% Point	360	360	340	
	(Railway)	Sulphur	(a)	0.15	0.05(d)	
Jet Fuel	A,A1,A2	Aromatics	22(b)	22(c)	22(c)	Reference (13)
		Sulphur	0.2	0.1	0.05	
Lt Fuel Oil	#2	Sulphur	0.5	0.15	0.15(e)	Summer

* CGSB specification 0.7 but refiners all have adopted a lower standard to meet engine manufacturer standards.

Notes:
(a) No federal standard.
(b) Can sell up to 25% with notification. Witn notification the smoke point can be as low as 18 as long as naphthalenes below 3%. Over 3% naphthalenes need 25 smoke point or 45 luminometer number (40 witn notification).
(c) No allowance above 22%, 3% naphthalene max. continues relative to 20 smoke point.
(d) A maximum 90% point of 340°C may also be established.
(e) Burning quality specification may be added tending to reduce aromatic content.
(f) May be stated as the equivalent of akylbenzenes with penalty for polynuclear aromatics (PNA's).

The odds on the suggested 1996 aromatic content changes becoming fact are probably in the order of 50 percent. The legislative controls over fuel specifications in Canada are very weak - currently only two provinces adhere generally to Canadian Government Standards Board diesel specifications. Major legislation reform, federally and by all provinces, will be needed to fully enforce any new standards. Here, we have assumed some delay in implementing such reforms, hence, the year delay compared to the U.S.

No change is seen in the diesel cetane number specification of 40 minimum, but the test procedure could well change to a more representative approach as a result of current evaluation work (3)(19)(50). Other test procedures may also be improved (100).

The refiner will not be able to blend precisely to the standards in effect at any time, so that his internal targets are expected to be about as following in 1996:

- Jet A: <0.04 wt percent S and <20 percent aromatics/<2 percent naphthalenes with burning quality still being the principal control (smoke point >20).
- Diesel fuel <0.04 wt percent S and <22 percent aromatics/5 percent PNA's with no aromatic control on railway diesel.
- Lt. Fuel Oil <0.12 wt percent S.

These sulphur and aromatics specifications are well below current production levels except for Jet A. The laboratory testing as well as process control precision levels will be much more precise than those now prevailing.

The very preliminary and, to a large extent arbitrary, nature of the forecasts of this section must be noted. The suggested changes are recorded primarily to provide a level for the aromatic saturation process market analysis.

3.5 PRODUCT DEMANDS

3.5.1 General

Table 3.5.1-1 summaries the NEB's domestic product demand forecasts, providing relevant breakdowns and ratios relative to middle distillate demands. The ratio of gasoline plus Jet B - (G) - to Jet A plus kerosene plus diesel plus lignt fuel oil - (D) - is most important to a refiner, as noted above.

As imports and exports and inter-regional transfers are important to understanding refinery balances in Canada, Table 3.5.1-2 outlines 1985 and 1986 transfers in the principal products. British Columbia has been shown instead of "West" as most imports/exports West of Ontario occur there. The Prairies have very little imports or exports and tne only significant flow is out to B.C.

3.5.2 Impact Analysis

Table 3.5.2-1 provides a very quick review of the principal changes anticipated in refinery demands and notes future concerns in the light of quality changes predicted in swings in product demands.

Light cycle oils have cetane numbers in the order of 25 and aromatic contents of 60 to 80 percent, even after conventional hydrotreating for product stability and sulphur reduction (91). Hence, they are the worst performers in all the middle distillate pool and the most concern in middle distillate blending. The predicted specifications do not include aromatics constraints on railway and marine diesel fuel nor on light fuel oil. Many refiners have the ability to segregate production and local distribution of much of their railway and marine diesel and lignt fuel oils - hence, the ability to blend off part or

TABLE 3.5.1-1
PRODUCT DEMAND DATA

Region	Year	NEB Scenario	Total Product $10^6 m^3$	Total Product % National	Ratios: Gaso+B / A+LFO/K+D	Ratios: LFO/K / A+LFO/K+D	Ratios: A / A+LFO/K+D	% of Total Products: A	% of Total Products: D	% of Total Products: LFO/K	Mid Dist.	Of Total Railway%	Diesel Marine%
Atlantic	1985	Actual	10.3	12.5	0.89	0.52	0.700	2	14	18	34	8.1	22.9
	1990	Low Price	10.8		0.79	0.48	0.076	3	16	17	36		
	1995	"	10.5		0.78	0.45	0.082	3	18	18	39		
	2000	"	10.7		0.77	0.41	0.086	4	20	16	40		
	2005	"	11.6		0.74	0.39	0.083	4	21	16	40		
	1990	High Price	10.9		0.78	0.49	0.074	3	16	17	36		
	1995	"	9.7		0.80	0.44	0.079	3	19	17	39		
	2000	"	10.1		0.73	0.40	0.079	3	20	16	39		
	2005	"	11.0		0.72	0.39	0.074	3	21	16	40		
Quebec	1985	Actual	18.1	21.9	1.25	0.46	0.13	4	13	15	32	11.7	--
	1990	Low Price	19.0		1.13	0.38	0.15	5	16	12	33		
	1995	"	19.5		1.20	0.30	0.16	5	17	10	32		
	2000	"	20.3		1.21	0.26	0.17	6	19	8	33		
	2005	"	21.8		1.21	0.24	0.18	6	18	7	31		
	1990	High Price	18.4		1.16	0.36	0.15	5	16	12	33		
	1995	"	17.4		1.21	0.27	0.16	5	18	9	32		
	2000	"	17.4		1.22	0.21	0.17	5	20	7	32		
	2005	"	17.9		1.24	0.18	0.18	6	20	6	32		
Ontario	1985	Actual	28.5	34.5	1.68	0.33	0.16	4	14	9	27	13.1	3.8
	1990	Low Price	30.0		1.61	0.28	0.17	5	16	8	29		
	1995	"	32.0		1.71	0.23	0.19	5	16	7	28		
	2000	"	34.1		1.70	0.20	0.19	6	17	6	28		
	2005	"	37.3		1.63	0.20	0.19	5	17	6	28		
	1990	High Price	28.4		1.65	0.26	0.18	5	16	7	28		
	1995	"	28.6		1.76	0.19	0.19	5	17	5	27		
	2000	"	29.0		1.75	0.15	0.15	5	18	4	27		
	2005	"	29.7		1.71	0.12	0.12	5	19	3	28		
West	1985	Actual	25.7	31.1	1.30	*	0.11	4	29	5	38	17.3	3.3*
(& North)	1990	Low Price	26.1		1.14	*	0.12	5	31	4	39		
	1995	"	26.8		1.09	*	0.12	5	32	4	39		
	2000	"	28.7		1.04	*	0.13	5	33	3	41		
	2005	"	31.1		0.97	*	0.13	5	35	3	43		
	1990	High Price	25.4		1.15	*	0.12	5	27	4	36		
	1995	"	25.4		1.09	*	0.12	5	33	3	41		
	2000	"	26.5		1.02	*	0.12	5	34	2	41		
	2005	"	28.0		0.95	*	0.11	5	36	2	43		
Canada	1985	Actual	85.6	100	1.35	0.31	0.12	4	18	10	32	14.4	5.8

Notes:

*Varies appreciably province to province: Man. 0.11, Sask. 0.17, Alta. 0.04, B.C. 0.19 in 1985
*Primarily in B.C. where 10.4% of diesel was for marine use.
Source NEB 1986 forecasts (69) and Statistics Canada 1986 data (88)(89).

Legend

B - Naphtha type Jet fuel - Jet B
A - Kerosene type Jet fuel - Jet A
LFO - Light Fuel Oil (primarily number 2 fuel oil) LFO/K - Light Fuel Oil plus Kerosene (= stove oil or no. 1 fuel oil)
D - Diesel Fuel

TABLE 3.5.1-2
NET PRODUCT TRANSFERS IN 1985 & 1986
10^9 litres

		1986(a)				1985(c)			
Region	Product	Produced	Net Exports	Net Transfer to other Region	Sales	Produced	Net Exports	Net Transfer to Other Region	Sales
Atlantic	Gasoline	3.729	0.964	0.340	2.710	2.983	0.190	0.108	2.720
	Jet B	0.258	0.087	-0.015	0.150	0.196	-0.025	0.025	0.196
	Jet A	0.122	-0.025	-0.124	0.310	0.122	-0.025	-0.078	0.253
	Kerosene	0.145	-0.042	0.006	0.153	0.167	0	-0.009	0.171
	Diesel	1.058	-0.347	-0.160	1.458	1.005	-0.270	0.124	1.488
	#2 Fuel Oil	3.007	1.143	0.158	1.648	1.887	0.231	0.142	1.705
	Hvy. F.O.	1.569	-0.921	0.118	2.368	1.322	-0.974	0.108	2.231
Quebec	Gasoline	5.983	-0.924	0.470	6.827	6.850	-0.485	0.581	6.773
	Jet B	0.014	-0.036	-0.026	0.075	0.111	-0.031	-0.004	0.078
	Jet A	0.647	-0.311	0.203	0.774	0.791	-0.174	0.251	0.766
	Kerosene	0.030	-0.179	0	0.168	0.173	-0.082	0.198	0.160
	Diesel	2.467	-0.402	0.396	2.513	2.557	-0.201	0.445	2.396
	#2 Fuel Oil	2.075	-0.016	0.105	2.422	2.343	0.198	-0.092	2.598
	Hvy. F.O.	1.918	0.042	-0.061	1.877	2.477	0.537	0.122	1.966
Ontario	Gasoline	11.228	0.190	-0.773	12.004	11.593	0.880	-0.614	11.837
	Jet B	0.153	0	0.047	0.127	0.129	0	-0.040	0.179
	Jet A	1.152	-0.092	-0.059	1.295	1.092	0.029	-0.163	1.244
	Kerosene	0.137	0.034	-0.029	0.130	0.101	0.020	-0.109	0.151
	Diesel	3.639	0.107	-0.426	3.955	3.534	0.145	-0.443	3.862
	#2 Fuel Oil	2.592	0.384	-0.249	2.220	2.842	0.761	0.027	2.303
	Hvy. F.O.	2.321	0.852	-0.084	1.163	2.540	1.084	0.066	0.845
B.C.	Gasoline	3.753	0.370	-0.408	3.600	3.875	0.712	-0.471	3.599
	Jet B	0.191	0.065	-0.011	0.145	0.179	0.059	0.004	-0.130
	Jet A	0.671	0.199	-0.001	0.461	0.469	0.062	-0.003	0.384
	Kerosene	0.059	0.003	-0.066	0.082	0	0.008	-0.075	0.070
	Diesel	2.183	0.320	-0.419	2.116	2.407	0.460	-0.428	2.250
	#2 Fuel Oil	0.417	0.007	0.039	0.367	0.490	0.040	0.019	0.437
	Hvy. F.O.	0.659	-0.079	0.010	0.749	0.653	0.042	-0.013	0.665

Notes: (a) Figures do not balance due to inventory changes.
(b) Figures underlined are over 20% of regional sales.
(c) Source Statistics Canada, Dec. 1985 & Dec. 1986 (88).

TABLE 3.5.2-1
1965 - 2005
OVERALL PRODUCT DEMAND CHANGES

Region	National Product Demand in '85 %	Change in Product Demand '85 - '05 %		G/D Ratio	MD in Total Domestic Production '85 - '05 %	LFO in Mid. Dist. '85 - '05 %	Jet A in Mid. Dist. (b) %	RWay + Marine Diesel of total MD in '85	Future Middle Distillate Concerns(c)(d) FCC LCO Disposal Problem (a)	Pour	G/D Ratio	Cetane & Smoke Point	Sulphur in Middle Distillate
Atlantic	12.5	+13	(+7)	.89->.74(.72)	34->40(40)	52->39(39)	7->8/(7)	31	Minor	Some	Hi	Minor	Yes
Quebec	22	+20	(-1)	1.25->1.21(1.24)	32->31(32)	46->24(18)	13->.8(18)	12	Some	Hi	--	Some	Yes
Ontario	34.5	+31	(+4)	1.68->1.63(1.71)	27->28(28)	33->20(12)	16->19(12)	15	Yes	Some	--	Hi	Yes
West (e)	31	+21	(+9)	1.30->0.97(0.95)	38->43(43)	negligible except B.C.	11->13(11)	21(h)	Yes(f)	Some	Hi (g)	Hi (g)	Yes

Legend:

NEB Low Price Case (NEB High Price Case)

_____ major change - - - - - - - significant change

Notes:
(a) FCC Lt. cycle oil production is in the order of 4 to 6% of total products in all areas - from 10 to 22% of total middle distillage. It is assumed here that railway and marine diesels can be up to 33% Lt. cycle oil - excess going to conventional diesel.
(b) Higher jet demand in all areas. But note need to review future crude mix to see if it may improve/worsen pour and smoke point concerns.
(c) Aromatics specifications in diesels will be major problems in all areas if predicted standard applied in mid '90's.
(d) Assumes '85/'86 product transfer patterns.
(e) B.C., Alta. Sask., Man., Yukon and NWT lumped together.
(f) Lt. cycle oil already blended into diesel on prairies - some segregation for railway possible and for Lt. fuel oil (in B.C. only).
(g) More S.C.O. equivalent to current Syncrude product, and/or Beaufort crude may meet NEB predicted decline in G/D ratio but will reduce cetane and smoke point.
(h) Note part of this supplied directly from Suncor oil sand operations.

all of their light cycle oil into these stocks insofar as sales permit in the region of the refinery.

Light fuel oil and railway diesels can contain up to about 30 percent light cycle oil and the latter will run about 6 percent of crude in the average refinery. In order to dispose of all light cycle oil outside road diesel, railway diesel and light fuel oil demands should total over 20 percent of total product demands to avoid problems. In practice, some light cycle oils end up as diesel in all regions due to refining and distribution system constraints.

The change in G/D ratio in the Atlantic region will require more hydrocracking of gas oil and/or middle distillate mode catalytic cracking, very uncommon now in North America, as well as the use of high middle distillate yielding imported crudes. Due to high railway and marine diesel and light fuel oil sales, as well as significant heavy fuel oil production, little light cycle oil is expected to be blended into road diesel in that region.

In Quebec, only a marked increase in Jet A demand appears a problem, but rapidly dropping light fuel oil demands may create a light cycle oil disposal problem in later years, pushing it into diesel in a major way. The lower middle distillate pool pour need is apparent from rising Jet A and diesel demands and falling light fuel oil needs.

In Ontario, the lower light fuel oil demand will pinch on light cycle oil disposal to products without aromatic constraints.

On the Prairies, most light cycle oil now goes into diesel, apparently satisfactorily, after some hydrogenation and cetane improver use where S.C.O. is used. But more S.C.O. will greatly increase pressure in this regard although it will also assist in lowering the G/D ratio. While the drop in the latter is quite pronounced, it is not expected to be a major problem.

B.C. product markets will be much more integrated with Alberta refineries in the future, hence B.C. is included here with Alberta.

3.6 REFINERY TECHNOLOGY CHANGES

3.6.1 General

The list of processes used in refining has not changed in the past 30 years, with the exception of residual conversion, light naphtha isomerization, and light olefin conversion. However, all processes have greatly matured with new catalysts contributing much to progress.

Over the next 20 years, major new breakthroughs in refining technology are not now evident - truly new processes only appearing occasionally. However, catalyst development can be expected to continue, especially in hydrotreating. Catalyst development, better design, and process control tools will lead to certain new process units looking little like their mid '50's versions.

Worldwide trends to reduced residual fuel oil sales and increasing middle distillate demands will emphasize the maximizing of middle distillate yields outside central Canada and the U.S. Continuing environmental concerns will phase lead out of most of the world's gasolines and reduce sulphur standards in diesel worldwide. Possible U.S. legislation constraining aromatics in diesel fuels could lead to similar restrictions in Europe and Japan in the late '90's. This study has noted a major surge in research and development of new catalysts and new approaches to the improvement of diesel quality.

Worldwide, crudes are expected to become poorer after about 1995 and this will increase residual fuel oil reduction and diesel quality pressures. Residual fuel oil reduction processes usually lead to poor quality light fractions, especially to higher aromatic content diesel fuel components. Some move to combination residual processes and to residual processes with better quality middle distillates can be expected.

Newer catalytic cracking catalysts tend to improve light cycle oils; but declining feed properties, particularly where reduced crude is charged, will offset such gains. Environmental pressures relative to sulphur emissions will continue to force U.S. refineries to look at hydrotreating of FCC distillate feeds. We expect that catalyst additives which absorb SO_x in catalyst regeneration and release the sulphur as H_2S in the reaction section, will overcome the problem in Canada in most cases. Thus SO_x emission concerns are seen as unlikely to result in improved quality FCC feeds and resulting better light cycle oil quality in Canada.

Operation of catalytic cracking units in a middle distillate oriented mode as opposed to conventional gasoline maximization can increase light cycle oil cetane number into the 30's. In this study only the Maritime refineries are seen as considering such an alternative. No major improvement in light cycle oil quality is foreseen in other areas.

Spent catalyst and chemical disposal concerns tend to favour low hazard catalysts and chemicals and long catalyst life in all processes. Chemical treatment of middle distillates appears likely to nearly disappear as product sulphur specifications drop, and raw middle distillate sulphur contents increase with time, partly offset by more S.C.O. and new frontier area low sulphur crudes.

3.6.2 Middle Distillate Options

In the past, refiners have not had to closely control middle distillate hydrotreating operations - the units usually have some "fat" in terms of desulphurizing capability and meeting product sulphur specifications has been relatively easy. An accuracy of say, ± 0.05 wt percent in most laboratory sulphur tests has been sufficient for process control. Reactor temperature control to ± 3°C has probably been the norm. However, new middle distillate quality standards will require accuracy levels of ± 0.01 percent and ± 0.5°C, respectively. These are attainable through new analytical and computer control techniques, albeit at a price.

The expected reduction in sulphur content of Canadian middle distillates, to meet the levels noted in Table 3.4-1 above, will require additional hydrotreating capacity at many refineries. Essentially all middle distillate components will require hydrotreating except synthetic derived materials.

For sulphur reduction to the expected levels, no need for pressure above 7.0 MPa (1000 PSIG) is expected in more than a few cases; although average pressures in middle distillate hydrotreating increase. Existing technology and catalysts will be satisfactory in all such cases, although prior pilot tests will be needed in many instances to confirm operating conditions and catalyst life. On-line and/or greatly improved laboratory sulphur testing will become essential.

For cetane improvement, expanded use of nitrate type cetane improver chemicals can be expected as the economics appear much preferable to alternate aromatic saturation and middle distillate hydrocracking approaches for up to 4 or 5 number improvement.

For a synthetic crude oil middle distillate, the following table reflects approximate current cost levels for cetane improvers.

TABLE 3.6.2-1
CETANE IMPROVER COST
S.C.O. Diesel

Improver Addition vol %	Cetane No. (a)	Approx. Cost of Improver Cents/Litre ($/Bbl)	Cost per Cetane No. bbl Cents/CNB
0.0	31	0.00 (0.00)	0.0
0.1	35.5	0.23 (0.38)	8.4
0.2	37.5	0.47 (0.71)	11.6
0.3	38.0	0.71 (1.13)	16.2

(a) Reference (55)

Response of light cycle oils is only to 50 to 60 percent of that for the S.C.O. reflecting the higher aromatic content of the light cycle oil (55). Light cycle oil will normally be used in blends with virgin diesel stocks and the response of the blend will tend to be better than that shown in the table.

Cetane improver will only be added in the amount needed in the particular diesel grade at the particular time. There is apparently no added NO_x emissions due to the use of the improver, but particulate emission will not be affected - they appear to be the same as those of the base fuel (80).

Unfortunately there is no acceptable jet fuel combustion quality improving chemical.

Extraction has been used in Europe for many years and was a common practice in North America many years ago to improve kerosene burning qualities. This study has not examined extraction as a route to Canadian middle distillate improvement. There appears some potential, at least for jet fuels, where the volume of extract will not be large and can be disposed of to railway diesels and/or light fuel oils.

The next section of this report considers hydrogenation routes to middle distillate upgrading. They appear the most likely candidates for major reductions in aromatic content and for cetane improvement.

3.7 PROCESS MARKET

3.7.1 General

This study has been confined to Canadian settings only. The previous "forecast" of diesel specifications indicates a phase down of sulphur before aromatic specifications become effective. It still remains to be seen if the latter will be implemented, but even if so, a four or so year gap is seen between the first sulphur reduction and an aromatic specification.

As will be seen later, the costs of saturating aromatics in middle distillates are very high, except for a few unique cases, due to very high pressure hydroprocessing as a minimum (18)(20)(26)(70)(101).

Until there is an aromatic specification for diesel, only kerosene going to Jet A is of concern relative to aromatics. Cetane will continue to be a major concern wherever synthetic crude oil is used; but control of blending, optimum use of existing special middle distillate hydrotreaters, possible partial use of hydrocracking capacity and continuing use of cetane improvers will generally obviate the need for new special diesel hydrotreaters except at Syncrude.

3.7.2 Short Term

JET FUEL

In the case of Jet A, reducing effective aromatic specifications will make the situation tight at certain producing refineries, especially those using synthetic crude oils or with residual conversion facilities. Aromatic saturation may be of short and long term interest in at least the following settings for both crude unit and hydrocracker kerosene intermediates:

- Suncor Tar Island Upgrader and/or using refineries
- Syncrude Upgrader and using refineries

A tightening of jet fuel sulphur specifications will result in all Jet A being hydrotreated. Few refineries not producing Jet A are expected to add such production. Only some revamp and newer catalysts are expected relative to tighter Jet A sulphur specification. Such changes will not impact on aromatic content, but will slightly reduce polynuclear aromatic content and probably increase combustion quality slightly.

While Jet A demands are projected to increase, the amount of such increase appears manageable and no more than three kerosene saturation units can be foreseen.

There are two refineries with bulk (naphtha plus kerosene) hydrotreaters that can probably achieve a 25 ppm or less sulphur content kerosene intermediate. There are also other hydrocrackers with kerosene and diesel product fractions at or below that sulphur level (but in several cases they may be more than 1 ppm of nitrogen). There may be interest in deeply saturating those low sulphur stocks in order that more Jet A can be produced than at present and/or the diesel pool cetane be increased, by blending poorer stocks (of higher sulphur content) with the low aromatic product from saturation.

DIESEL

The costs of hydrotreating any middle distillate stock to a 0.05 wt percent sulphur content are significantly less than saturating its aromatics. The time gap between new sulphur and new aromatic specifications appears to indicate a definite trend to meet only the former in new hydrotreating capacity - it will be more economic to add a second saturation stage/unit at a later date when the necessity is apparent.

Conventional hydrodesulphurization will saturate a portion of the PNA's present providing a slight cetane increase in most cases.

There may be the odd case of a new diesel hydrodesulphurization facility being planned for future aromatic saturation and significant cetane improvement, but not necessarily operated other than for sulphur reduction until cetane improvement is economic - e.g. due to better economics of added S.C.O. use- and/or when lower aromatics are mandatory. At this time, the future use of a mild middle distillate hydrocracking approach discussed later appears most likely in such cases than aromatic saturation due to cetane maximization concerns. This very preliminary conclusion extends to both refineries and Syncrude.

This five to nine year scenario shows potential for only two or three kerosene oriented middle distillate aromatic saturation units. These would most likely be installed in synthetic crude oriented settings.

3.7.3 Long Term

If and when aromatic specifications are announced for diesel fuel, there will be very hard looks at maximizing light cycle oil in products without aromatic specification including light fuel oil, heavy fuel oil and marine diesels. Tighter sulphur specifications on all middle distillate products will force deeper hydrotreating of light cycle oil (but only to the 4.8 or 5.5 MPa level). This will improve stability and combustion properties generally, allowing slightly higher concentrations of light cycle oil in light fuel oil and railway diesel (assuming these products to have no aromatic content specifications).

In the Quebec and Atlantic regions, aromatic reduction in middle distillates will be primarily confined to conventional crude fractions. In Ontario and B.C. more light cycle oil will need to be processed and essentially all will be processed on the Prairies. Due to the economics of scale and reduced process severity compared to light cycle oil, blends of conventional and/or synthetic crude diesel fractions and light cycle oil appear the most likely feed in Ontario and the West. No more than one or two pure light cycle oil saturation units are foreseen, and there may well be none.

If a diesel aromatic specification is imposed, virtually all refineries will need aromatic saturation units. The smaller refineries may "purchase" low aromatic blending stock from another refinery much as Shell Burnaby can do at this time from Shell Scotford and presumably Petro-Canada at Port Moody will do in 1988. Thus, B.C. refineries, in particular, are not considered as having high potential. Shell Scotford, Petro-Canada Edmonton and Co-op/NewGrade will already be well situated. Shell can be expected to expand use of their own saturation processes, if needed, in any case (85). Irving use gas oil hydrocracking for part of their middle distillate and may get by due to high light fuel oil sales. This leaves the following:

- Esso - Strathcona (Edmonton), Sarnia, Dartmouth
- Petro-Canada - Edmonton (Conventional crude)
  Mississauga/Oakville, Montreal
- Turbo - Balzac (Calgary)
- Suncor - Sarnia
- Texaco - Nanticoke, Dartmouth
- Ultramar - St. Romauld

Syncrude appears most likely to continue with a mild hydrocracking route, due to continuing need to minimize middle distillate yield and maximize cetane. At least half of the above refineries would likely use the same approach due to its inherent cetane gain and no need to maximize middle distillate yields, as well as a capability of processing more S.C.O.

There may be continuing interest at three of the refineries noted above in section 3.7.2 above relative to deep saturation units on selected low sulphur feedstocks to allow blending off of high sulphur, high aromatic stocks.

Thus, if an aromatic specification is added to diesel fuel standards, this study anticipates two to five new Canadian diesel saturation units with blended light cycle oil/straight run middle distillate feed. In parallel, or as alternatives, one or two low sulphur kerosene feedstock saturation units may develop (if not built in the short term).

3.7.4 Summary

In the short term, new interest in middle distillate aromatic saturation is seen at only a few refineries - those producing Jet A from synthetic crude and similar feedstocks. A potential for one to three kerosene boiling range feed units is foreseen in the next five to nine years.

If a diesel aromatic specification is imposed in the middle '90's, the potential for aromatic saturation of middle distillates increases dramatically, although in several cases the selected process may incorporate some mild hydrocracking to increase cetane beyond that possible with aromatic saturation. Aside from Shell, who have their own technology, a total of roughly ten new units would be required, depending to a significant extent on whether a major Syncrude expansion proceeds and if so, what form of middle distillate hydrotreating is used there. Of tnese, possibly half would be mild hydrocrackers, the other saturating aromatics only.

Tne likely imposition of tighter sulphur specifications on diesel by the early '90's is not expected to impact on the above noted potentials to a major extent, but will provide low sulphur content (0.05 to 0.15 weight percent) feedstock for aromatic saturation.

Any aromatic saturation process will face appreciable competition as discussed in the next section.

4. AROMATIC SATURATION PROCESSES

4.1 PREAMBLE

As noted above, the refiner has the following options to improving middle distillate combustion qualities and reducing aromatic content:

- cetane improver (diesel fuel only) without aromatic reduction,
- more selective crude usage and processing - e.g. block mode,
- pressure on S.C.O. producers to improve their products,
- extraction to remove all or portion of aromatics, and
- hydroprocessing using selected catalysts (1)(25)(26).

This section discusses the latter alternate. For ease in discussion only, the hydroaromatic saturation routes have been divided into the following general categories:

Type I	-	Precious Metal Sulphide Catalysts
Type II	-	Other Precious Metal Catalysts
Type III	-	Nickel Catalysts
Type IV	-	Miscellaneous Catalysts
Type V	-	Conventional NiMo and NiW Catalysts
Type VI	-	Mild Middle Distillate Hydrocracking Processes

While this study's terms of reference, excluded other than the Types III, IV and V routes, it is essential to have an understanding of the respective niches of all routes. However, this study concentrates on Type III and V routes in its detailed analyses, with a single Type II reference point.

There is very appreciable research and development work in progress at this time relative to middle distillate catalytic processes for desulphurization, denitrogenation, and cetane improvement, as well as for aromatic saturation (14)(25)(26). The use of several different catalysts in the same reactor is being promoted as is the combination of various catalytic functions on the same catalyst. One developer has noted that its newer hydrotreating catalysts are as much as seven times more active than the 1950 equivalents. Hence, continuing development and life and activity improvement of even the current standard catalysts must be noted.

The current development activities are especially important to the case of aromatic saturation. The need for much deeper desulphurization process decisions may be two to five years away, whereas most diesel fuel aromatic reduction decisions will not be necessary for another five to six years at least. Refiners definitely prefer to buy proven catalysts and processes; this infers a lead time of at least three years from successful pilot plant testing before full scale commercial acceptance.

As most catalyst and process details are proprietary, publicly available data are usually scarce. Herein, only data publicly available or specifically cleared for use is presented.

4.2 HYDROPROCESSING ALTERNATES

4.2.1 Type I Precious Metal Sulphide Catalysts

The Unocal Unisar process with its platinum sulphide catalyst is the only identified example in this class. The sulphur of the feedstock must be converted to H_2S prior to the platinum catalyst reactor. This is done with a conventional hydrodesulphurization catalyst bed in series. Both reactors will operate at their own optimum temperatures with inter-reactor cooling, but both operate at the same 4 to 7 MPa pressure. The process is claimed to be able to reduce aromatics to a very low level, but this brief review doubts economic use below 5 to 7 percent aromatics in kerosene.

Unocal claims the process can take up to one weight percent sulphur in the feed, the operating pressure being increased to provide more hydrogen partial pressure. The process appears well proven on kerosene boiling range feedstocks. The catalysts are regenerable. Sensitivity to organic nitrogen compounds is unknown but, at the conditions of the hydrodesulphurization step, most organic nitrogen compounds will be converted to ammonia.

4.2.2 Type II Other Precious Metal Catalysts

Virtually every precious metal catalyst manufacturer has one or more catalysts that can reduce aromatic content to very low levels, generally platinum based (1)(46). Sulphur tolerance is probably in the order of 5 to 15 ppm and 5 ppm or less of nitrogen (6). One manufacturer noted current development of a form capable of handling up to 150 ppm of sulphur and early commercialization is considered likely.

UOP licence their AH Unibon process for middle distillate aromatic saturation and its capital costs will be noted later. To date, most refinery type applications have been for solvent and kerosene fractions (51).

These catalysts have long been used for benzene hydrogenation, jet fuel aromatic saturation, and for kerosene boiling range solvents (45)(99)(118). The Shell Fort Saskatchewan middle distillate hydrogenation unit is in this class and Shell have a similar system for solvent hydrogenation in Sarnia. The Kemtek Montreal East cyclohexane unit originally had a UOP platinum catalyst. It is not clear if that unit will be restarted.

Operating pressures are comparable to that used by CANMET in its nickel catalyst work - below 4.0 MPa - and reaction temperatures are in the 140 to 200°C range (17).

There is a concern about isomerization in the case of benzene saturation and, hence, the catalyst support is of high purity alumina. Platinum catalyst is preferred to nickel if high reactor temperatures are needed due to ring opening with nickel. Wile the platinum content can vary, approximately 0.3 wt percent appears to be the norm.

ARCO's Watson California coker kerosene unit has had the same platinum on alumina (monometallic catalytic reforming) catalyst in use for the past 20

years. This unit uses a two reactor pretreatment system to saturate olefins in the feed and remove sulphur and nitrogen to very low levels (99). The unit is currently undergoing its second expansion but no reactor or catalyst changes are planned.

These catalysts are all regenerable and sulphur and nitrogen are temporary poisons only.

While platinum is expensive, its cost is carried as an inventory as over 90 percent will be recovered whenever the catalyst is returned for reprocessing. A typical catalyst is in the order of $46.00 Cdn. a pound, including 0.3 weight percent platinum, assuming about $U.S. 600 per troy ounce. (During the study, the platinum price fluctuated from below $U.S. 500 to over 600 an ounce.)

4.2.3 Type III Nickel Catalysts

Nickel catalysts are used interchangeably with platinum for many hydrogenations, the selection depending upon the economics of the day (96). Nickel is more sulphur and nitrogen intolerant than platinum - virtually any sulphur or nitrogen irreversibly poisons nickel catalysts (6).

United Catalysts Inc. list two Exxon developed nickel based catalysts for benzene and kerosene saturation, both have copper (4.4 percent) and one has cobalt (5.0 percent) (25). These catalysts were developed to minimize hydrocracking - a major concern with nickel catalysts - and to allow activation at a lower temperature. The catalyst with cobalt provides a minor degree of sulphur tolerance. There is work underway relative to promoting nickel with Group VIII metals as appreciable synergy has been noted in certain applications (83)(86). Further investigation in this regard appears warranted, but the two current challenges of sulphur intolerance and non regenerability must be kept in mind (6).

The industrial hygiene, safety and environmental concerns of using nickel catalysts are discussed in Appendix A.

4.2.4 Type IV Miscellaneous Catalysts

This category covers a wide variety of approaches - most very new and/or untried in the refining industry. Virtually all data are proprietary and few hard reportable facts are available. In two instances, catalysts that have been used outside refining will shortly be introduced, at considerable saving in development costs but with a need to demonstrate performance to the oil industry. One of these catalysts is said to operate at lower temperatures than conventional catalysts.

Trimetallic catalysts are being developed containing the desulphurization capability of cobalt with the saturation capability of other metals in association with molybdenum. Certain of these may be available for testing at this time. Current rapid advances in catalyst fundamentals should prove of major importance in developing such multimetal catalysts as well as other middle distillate oriented catalysts (14)(41)(63).

The use of two catalysts in separate layers has been noted in the trade literature and was a frequent comment by many contacts and is not a new concept in refinery hydrotreating (2).

4.2.5 Type V Conventional NiMo and NiW Catalysts

While hydrodesulphurization and hydrodenitrogenation with cobalt molybdenum (CoMo) and nickel molybdenum (NiMo) catalysts at pressures below 10 MPa will provide significant saturation of all but one ring of PNA's, the total aromatic content as measured by volume is little reduced. Higher pressures and newer, more saturation active, nickel molybdenum or nickel tungsten (NiW) catalysts are required to provide bulk reduction of the volumes of total aromatics present (23)(34)(63)(110)(111)(112)(113)(122).

Pressures as low as 4 MPa can be used to achieve a 0.05 wt percent sulphur level with CoMo catalysts, even with difficult feeds such as light cycle oil. Pressure has little effect on desulphurization until the part per million level is needed as with platinum and nickel catalysts. Thus future desulphurization needs can be met at conditions much milder than needed for reduction of aromatics using CoMo and NiMo catalysts. As CoMo catalyst is not particulary active relative to saturation, only NiMo and NiW catalysts will be considered here. As ring saturation generally follows nitrogen removal, the catalyst needs to have good denitrogenation properties (5).

Newer versions of conventional NiMo and NiW hydrotreating catalysts are now available that promise reasonably good saturation at pressures in the order of 10.3 to 11.0 MPa. Use of CoMo hydrodesulphurization catalysts in series with better saturation catalysts is feasible as long as heat is removed between the reactors to minimize equilibrium impacts during aromatic saturation. Possibly more active hydrodesulphurization catalysts will overcome this challenge - but as removal of ring nitrogen occurs before saturation of all rings in a particular compound, a good denitrogenation capability is also needed.

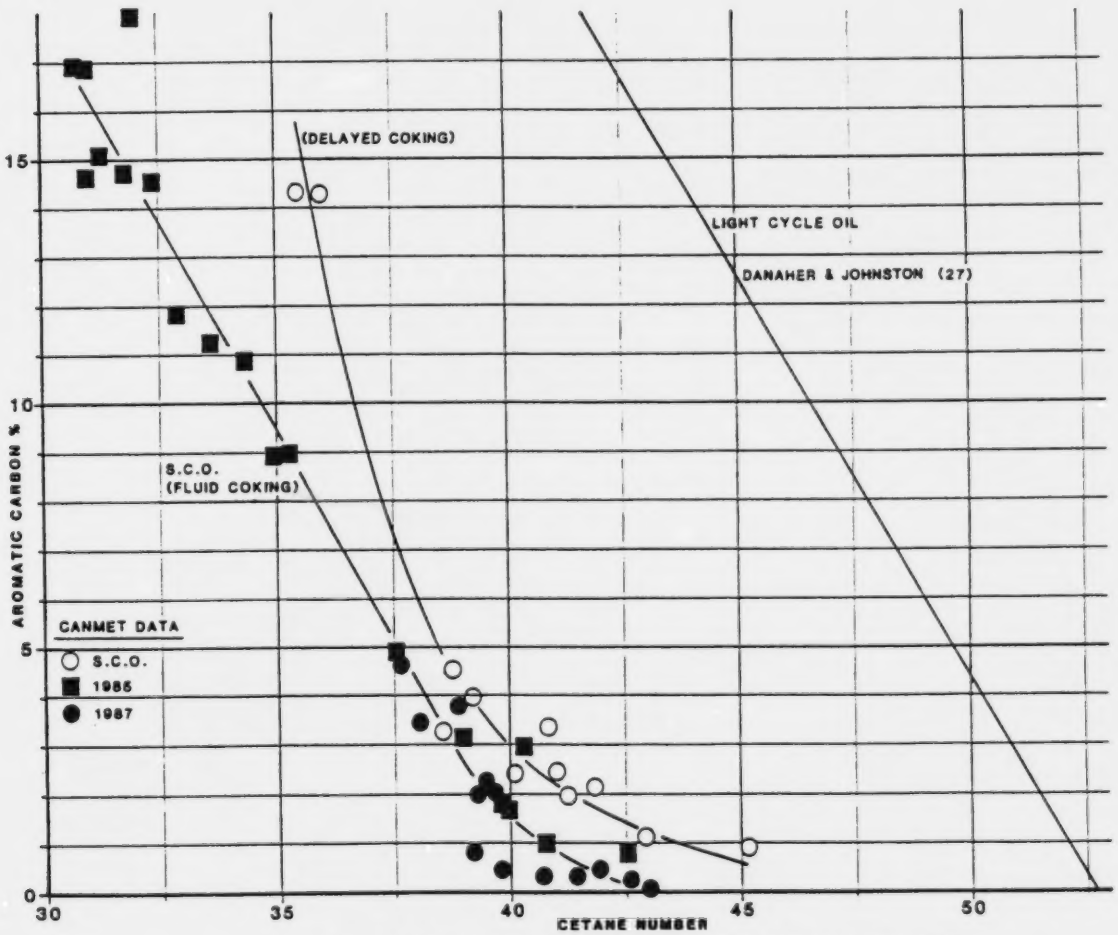
Equilibrium conditions greatly favour lower temperatures - the opposite of desulphurization. Kinetics have been explored in depth by a number of investigators (8)(9)(49)(122)(123)(124). In this regard, use of NiMo and NiW catalysts for the saturation of aromatics to very low levels in specialty oils is to be noted, although this is normally done at very high pressures - e.g. 25 MPa. Certain newer catalysts have been developed to maximize saturation and in a few cases replace those tested by Simmons and Deutscher for CANMET (84). Various references do not necessarily agree with each other - e.g. (58) and (121) - and pilot tests that replicate commercial operation on the specific catalyst processing the specific feed are essential in all cases (120).

While NiMo catalysts are being improved in their aromatic saturation capability, so are the NiW catalysts; thus, it is largely of economics which catalyst is selected for a given service.

4.2.6 Type VI Mild Middle Distillate Hydrocracking Processes

Raising the temperature when using the conventional NiMo and NiW catalysts above those needed for hydrodesulphurization leads to hydrocracking of portions of the middle distillate with the daughter compounds being significantly higher in cetane (10)(43). While aromatic reduction is poorer due to the higher temperatures, the PNA reduction to monoaromatics is generally good. The partially saturated multicyclic compounds appear to crack in a saturated ring next to a residual aromatic ring.

Figure 4.2.6-1 is taken from CANMET hydrogenation data for fluid and delayed coking and compared with a portion of Dehaner and Johnston's recent curve of cetane vs. aromatic carbon content for saturation of a light cycle oil (27). The synthetic middle distillates obviously have marked differences in base composition compared to the light cycle oil. In cases with mild hydrocracking, the slope of the curve will be less pronounced due to formation of higher cetane daughter products through cracking reactions.



VARIATION OF AROMATIC CARBON WITH CETANE NUMBER - A COMPARISON OF SYNTHETIC CRUDES WITH LCO

FIGURE 4.2.6-1

Special catalyst formulations, such as addition of fluorine and other promoters and use of a silica base, can provide enhanced hydrocracking activity. Such catalysts can be used in a conventional hydrocracker as first and second stage catalysts in the hydrocracking of gas oils.

For middle distillate upgrading the first stage catalyst in a hydrocracker is used almost exclusively, the second stage hydrocracking catalyst being used only for gas oil hydrocracking at which time the first stage provides desulphurization and denitrogenation capacity only. Gulf was an early promoter of mild hydrocracking of S.C.O. middle distillates and light cycle oils to improve the cetane beyond what can be accomplished by saturation alone (10)(43). At both Petro-Canada in Edmonton and NewGrade in Regina, conventional hydrocracking was desired in any case and dual purpose units evolved. Both units can process blends of light cycle oil and S.C.O. middle distillates up the 42 to 45 cetane level when operated in the middle distillate upgrading mode. NewGrade is using proven Unocal catalysts in their new unit.

A mild middle distillate operation requires more capital due to the slightly higher pressures and significantly higher temperature than in the Type IV operation. Added costs are also required due to added product recovery facilities, and occasionally, more exotic metallurgy in the product recovery system due to presence of fluorine promoter compounds.

The mild hydrocracking route, while expensive, will yield more total liquid products than any other route. The cracking produces up to 15 percent naphtha of a good quality for catalytic reforming, with middle distillate yield above 90 percent. The economics for such processing will be best in the west where natural gas for hydrogen is available at a low cost.

4.3 ADSORBENTS

A least two process licensors of catalytic reforming processes recommend adsorbents prior to the reforming system to remove traces of sulphur in the feedstock in order to optimize the platinum rhenium bimetallic reforming catalyst. The use of adsorbents in benzene production, on recycle gas, is not unknown; and use of zinc oxide as a sulphur adsorbent, already common in ammonia production, is being extended to natural gas and light liquid hydrocarbons (15).

At the current stage of zinc oxide adsorbent development no capability is shown for thiophenic sulphur, except at temperatures well above those of most hydroprocessing processes. Adsorption of H_2S down to room temperature is, however, becoming common and with prior hydrodesulphurization, zinc oxide can be used to adsorb the last traces of H_2S and light mercaptans (6). This could be an advantage following middle distillate HDS where some recombination of H_2S and olefins to form mercaptans can be anticipated.

One licensor recommended the use of a nickel type adsorbent before any nickel saturation catalyst to protect the latter from any upsets in the prior feed desulphurization. The use of nickel adsorbents has been assumed here before a nickel saturation catalyst, as these have the ability to disassociate thiophenic and other sulphur compounds, with the sulphur essentially irreversibly adsorbed.

At least two catalyst manufacturers provide special nickel catalysts, to adsorb sulphur compounds when operated in liquid phase at 150 to 200°C. These adsorbing catalysts have essentially zero leakage of sulphur compounds until breakthrough occurs at the 15 to 20 percent loading level. The two beds are used in series to insure full pickup of sulphur.

The nickel catalyst used in the CANMET work to date, and its equivalents, do have similar adsorbent capacities but tend to "leak" sulphur with the rate rising as the amount adsorbed on the catalyst increases.

The adsorbing nickel catalysts are expensive at about $27 Cdn. per kilogram equivalent to over $100 per kilogram of sulphur adsorbed ($10,000 per tonne). There may be a minimal credit from the metal reclaimed from the spent catalyst but less than 10 percent of the original catalyst cost even without any freight charges.

The high cost of adsorbent makes its use without prior HDS impractical except in a few unique settings.

4.4 SATURATION PROCESS SELECTION TODAY

While future economics and catalysts available at the time will determine which aromatic saturation process route is selected, some generalities can be made relative to the current situation.

Figure 1.6-1 of the Synopsis provided a brief overview of the ranking seen for the approximate attractiveness, at this time. Note that the Type IV process catalysts have not been considered as no public data are available.

Type I Precious Metal Sulphide	Process appears to fit in well, above the sulphur in feed level at which other precious metal (platinum) and nickel catalysts require desulphurization, and below the sulphur level at which there is too much sulphur for integral desulphurization/saturation. Organic nitrogen and ammonia tolerances require definition and proven operation on full boiling range diesel may be needed.
Type II Other Precious Metals	These normally platinum based processes fit up to their sulphur and/or nitrogen tolerance levels. While platinum is expensive and likely to continue to rise in cost, it is regenerable and, hence, only initial cost is important. Sulphur and nitrogen compound tolerances need to be well defined for the particular feedstock. With platinum catalysts very low levels of aromatics can be achieved due to high activity at low reaction temperatures. Here we assume an upper sulphur limit of about 15 ppm today (and 150 in '88).

Type III Nickel

When the sulphur and nitrogen levels of the feed are already below 1 ppm, nickel will be the current economic choice for aromatic saturation, with product quality essentially the same as for Type II catalysts. However, in order to compete with that class at sulphur levels up to approximately 10 ppm, prior nickel adsorbents are needed (assuming nitrogen is not a problem). Even then, the use of spent catalyst as adsorbent before the formal adsorbents will be needed to minimize costs.

The economics of both platinum and nickel routes are likely to be poor until the upper sulphur and nitrogen tolerances of the platinum sulpnide route are reached. At that point all three routes will require prior desulphurization and denitrogenation in separate facilities.

The lack of regenerability is a major deterrent to use of the nickel route, as it introduces significant catalyst disposal challenges.

A process of the I, II or III type will be used where very low aromatic contents are desired, but will compete with type IV catalysts over about 10 volume percent aromatics in the product.

Type IV Conventional NiMo & NiW

Such catalysts appear likely to fit only with feedstocks above about 5000 ppm of sulphur and for situations requiring aromatic reduction only to the 10 to 20 percent volume level. Over about 5000 ppm of sulphur special bulk hydrodesulphurization capacity may have to be added.

Type VI Mild Middle Distillate Hydrocracking

This route is a logical choice at S.C.O. production and using refineries to increase diesel quality - cetane - and to partially correct the very high middle distillate yield. However, the route is more expensive than the others available relative to aromatic saturation, per se. It will probably only be used for full boiling range diesel fuel operation. Use for kerosene "upgrading" appears unlikely as normally only a mild improvement is needed, using types I, II, III or IV catalysts at less cost.

5. PROCESS COMPARISON

5.1 PREAMBLE

In order to assess the merits of the nickel catalyst aromatic saturation route in the improvement of Canada's middle distillates, a comparison has been made for four feedstocks looking at the nickel route versus a conventional NiMo hydrogenation approach.

The use of platinum based alternate routes has not been examined in any detail, but data for one comparable case were provided by a licensor and are noted later. Mild hydrocracking for cetane improvement and aromatics reduction has also not been considered herein, but facility costs in such a route will be higher than those of the NiMo route due to higher temperatures and more expensive metallurgy. The "conventional" route has been represented here by a mild temperature, high pressure NiMo on alumina operation (with very minimal cracking).

The common objectives of the alternate process facilities considered have been to have a product below 20 volume percent in total aromatics content and below 0.05 wt percent sulphur. In practice, increasing smoke point (or luminometer number) will be more important in today's scene relative to jet fuels, and cetane number relative to diesels. The 20 percent aromatics standard exceeds predicted specifications but is considered a realistic level for process design purposes allowing processing of poorer feeds on occasion.

A basic 2000 m^3/d of feedstock has been assumed available in all cases, except a light cycle oil case for which 1000 m^3/d was selected as a more realistic size. Consideration has been given to deeper saturation in cases where this would reduce the feed to the new units - the unprocessed material being blended back.

Existing mild hydrotreating capacity exists in virtually all Canadian refineries for light cycle oil and in many for blended conventional crude light gas oils (kerosene/diesel boiling range) and light cycle oil. As will be discussed below, use of such capacity has been assumed herein.

5.2 FEEDSTOCKS

5.2.1 General

The following four feedstock cases were recommended and accepted by the CANMET scientific authority for comparison of conventional (NiMo) processing and the nickel based route being developed by CANMET:

- Suncor "Kerosene" — Representative of a stock whose market value could improve through aromatic saturation and of a specific scenario at the Tar Island plant. Also representative of poorer kerosenes that might be candidates for improvement to jet fuel quality.

- Syncrude Middle Distillate
  The primary synthetic middle distillate now used by Canadian refiners (22)(44)(66)(109)(114)(115)(122).

- Straight Run (Light) Gas Oil/Light Cycle Oil Blend
  Representative of a very common coprocessing situation in conventional refinery hydrotreating.

- Light Cycle Oil
  Representing the most highly aromatic and most difficult to upgrade of all Canadian refinery middle distillate components.

These four cases provide a broad spectrum of reference points for analysis of aromatic saturation of other Canadian refinery and upgrader middle distillate streams. Current conventional crude fractions will normally be easier to process than the above streams. But their kerosene - Jet A - fraction is usually just inside or very close to current jet fuel aromatic and combustion property specifications, and their diesel components only 10 to 20 percent higher in aromatics than possible new specifications, hence they may be blended off with the product from a saturation unit.3

TABLE 5.2.1-1
FEEDSTOCK QUALITIES
(a)

Characteristic	Units	Suncor Kerosene	Syncrude Mid Distillate (1989)	Blend-Virgin Gas Oil (70%) - L.C.O. (30%)	Light Cycle Oil
Pretreatment	--	none	none	Bulk Hydrotreat	Bulk Hydrotreat
Gravity	°API	36.5	30	32	20
Sulphur	wt ppm	200	400	2000	3000
Nitrogen	wt ppm	20	135	30	100
Cetane	Number	35	32	40	22
Aromatics	Vol %	30(e)	36	39	70
Composition(b)				(c)	(c)
Paraffins	wt%	26.1(e)	12.5	32.8	18.4
Naphthenes	wt%	41.0(e)	52.1	26.4	8.5
Monoaromatics	wt%	20.6(e)	27.6	17.9	17.6
Ring Aromatics	wt%	10.4(e)	6.5	21.5	53.1
3+ Ring Aromatics(d)	wt%	1.9(e)	1.3	1.4	2.4

Notes: (a) Varying compositions in all cases - average or assumed data shown.
(b) Sulphur and nitrogen compounds included with hydrocarbon components.
(c) References (91) and (93) used for bases but wide ranges of data again noted for light cycle oil.
(d) Only trace of 4 ring aromatics present.
(e) Design figures at peak aromatic content.

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[3]References (64)(65) and (97) are typical references to other oils and/or shale derived middle distillate testing.

5.2.2 Prior Processing in Blend and Light Cycle Oil Cases

Analysis of alternates to aromatic saturation in existing refineries indicates that light cycle oil hydrotreating facilities exist in all but 2 or 3 significant refineries, often in conjunction with virgin diesel fraction hydrotreating. In reviewing the "conventional" versus nickel routes to aromatic saturation it is noticed that the economics of both routes can be improved and the new units simplified if the existing low pressure - all below 6.3 MPa (900 psig) - hydrotreaters were used to prepare at least the light cycle oil to the new units.

The NiMo operation is anticipated to be at relatively low temperatures with limited desulphurization capability. Denitrogenation will be important due to the need to remove most cyclic nitrogen before final aromatic saturation. The NiMo catalyst selection will be targeted at aromatic saturation which precludes use of normal desulphurization temperatures due to equilibrium considerations. Thus in order to handle high sulphur olefinic feedstocks, a pretreatment stage is needed in any case before the saturation unit.

The use of such existing facilities in the Blend and Light Cycle Oil cases eliminates the need for a prior (or post) high temperature desulphurization stage in the NiMo route and a significantly expanded desulphurization stage in the Ni route. The use of existing mild hydrotreating facilities will also greatly improve the life of catalyst (in at least the first bed) in the new units due to prior saturation of olefins in cases with light cycle oil. Less exchanger fouling will also result in all cases.

Herein, it is assumed that existing mild hydrotreating facilities are used to prepare feedstock for saturation in both the Blend and Light Cycle Oil feed cases.

5.2.3 Suncor Kerosene

The particular stream exists only at the Suncor oil sand plant. That plant has three hydrotreaters processing naphtha, kerosene, and gas oil fractions of the coker distillate and virgin bitumen components. The "naphtha" unit feedstock contains some components boiling in the kerosene/diesel range and the gas oil hydrotreater produces appreciable diesel boiling range material, part of which, the gas oil sidestream (GOSS), is sold as a separate railway diesel product. The naphtha, kerosene and gas oil products, except for GOSS, are blended in ratios to suit each user. Thus, the middle distillate a refiner fractionates from a Suncor synthetic crude oil blend will differ from the "kerosene" feed assumed here.

The word "kerosene" in this case is, to some extent, a misnomer as the product boils from 190 to 340°C, above the normal end point for conventional kerosene. However, with a 50 percent point of about 250°C, this stock is only marginally higher in boiling range than many Canadian conventional kerosene intermediates.

Much of this "kerosene" boils in the Jet A range but its aromatic/naphthenic nature precludes such use at this time. If the aromatics could be reduced,

direct jet fuel production would be possible at using refineries without need for conventional crude blending stocks4. For a diesel blending component, lowering the aromatics to the 20 percent level will probably not raise the cetane number to 40, but will significantly reduce the amount of cetane improver required to meet that specification in any case.

Processing of this stream would most likely be done at Tar Island but could also take place at using refineries in Ontario and British Columbia (along with other Suncor middle distillate components). In refinery settings only a jet fuel component is likely to be processed in the near term. In the long term, when aromatic specifications extend to diesel, a full diesel fraction might be considered at the using refineries. This may involve a slightly more aromatic feedstock than shown here as noted above.

The recent expansion announcement of Suncor indicates no significant change likely in "kerosene" product quality over the next five to six years as no new upgrading units are planned.

However, it is to be noted that there are quality fluctuations from time to time in the Kerosene Hydrotreater (KHT) product, particularly as regards sulphur. Also, as with all fixed bed systems the KHT catalyst activity declines through the run and there will be a tendency to more thermal cracking and a lighter product towards the end of the run. The bitumen feed to the coker also varies in quality, affecting the KHT feedstock to a minor extent. Allowances must be made in design to handle sulphur up to 500 ppm and higher aromatics on occasion. A 30 volume percent aromatic feed is assumed here.

The Suncor "kerosene" will be more difficult to process than many conventional crude kerosene fractions, but is the "easiest" of the four cases considered here. As will be seen later, difference in costs between a milder operation and that needed by the Suncor "kerosene" will be quite minor and largely related to hydrogen consumption. In the Ni case, only 40 percent of the "kerosene" is assumed processed, but to a level of <5 percent aromatics. The processed material is blended with the untreated feed to provide the final product.

5.2.4 Syncrude Middle Distillate

In the current Capacity Addition Project, a new middle distillate hydrotreater is being installed to process feed from bitumen distillation and from the new LC Finer. It will not process middle distillate from the existing gas oil hydrotreaters. The new middle distillate unit will be on stream in September of 1988.

The timing of a Syncrude decision to proceed with a major expansion is unknown, hinging on oil price projections, taxation and other government policies as

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[4]This assumes that lowering the aromatic content of the Jet A portion of the stream will raise the smoke point to acceptable levels; review of the available data indicates this is very likely but confirming pilot plant work is needed.

well as on owner internal economics and cash flows. However, if a major expansion proceeds, current indications are that aromatics in middle distillates will likely go below the 20 percent level. A major expansion project is not expected to be on stream before 1993, in any case; hence, has not been considered here.

There is a significant uncertainty about long term interests in processing Syncrude middle distillate in aromatic saturation units at Syncrude or at using refineries. The case considered here represents a near term, 1989 through 1994, outlook. Again, in the Ni case a portion of the feed - 45 percent - is bypassed around the saturation unit to be blended with a low 25 volume percent aromatic saturation unit product.

5.2.5 Blend

Currently it is very common practice to coprocess virgin middle distillates, particularly the heavier fractions, with light cycle oil, with up to 30 percent of the latter for diesel fuel and light fuel oil blending stocks. The coprocessing results in an easier to control unit as a result of less heat of reaction due to olefin saturation and desulphurization, and less exchanger and catalyst fouling due to a more saturated feedstock compared to processing light cycle oil on its own.

As noted in section 5.2.2, continued use of existing hydrotreating facilities is assumed in this study to provide a stable, partially desulphurized feedstock for either NiMo or Ni routes to aromatic saturation.

The characteristics of feedstocks to "blend" aromatic saturation facilities will probably show major swings in aromatic content, distribution of aromatics by type, and in sulphur and nitrogen content due to variations in crudes, crude distillation cut points, amount of light cycle oil processed, and FCC operating parameters. A saturation unit operating on a virgin/light cycle oil blend feedstock will need to be able to process virtually any feedstock except 100 percent light cycle oil. The selected 30 percent of light cycle oil represents a relatively severe operation compared to a more "normal" 20 percent or less.

Herein, when light cycle oil is considered for aromatic characteristics, an "average" light cycle oil is assumed with gravity of 20° API and 0.3 weight percent sulphur. The averages used are considered realistic but a large variance, refinery to refinery and even day to day, at individual refineries is to be noted in total aromatics and the distribution of aromatics.

Saturating aromatics in the blend to the 20 percent level will normally bring the cetane number of the blend above 40.

While there is some potential to bypass part of the feed around a Ni saturation unit, the amount is not great and constrained by both sulphur and aromatics. Hence, total feed at 2000 m^3/d has been assumed for both NiMo and Ni approaches with 20 percent aromatics in both products.

5.2.6 Light Cycle Oil

Certain Canadian refineries hydrotreat light cycle oil on its own, but such units are specially designed for high heat of reaction (reduced furnace duty) and for the significant fouling potential of the feedstock.

When the catalytic cracking unit is operating in a gasoline mode, light cycle oil is produced at a rate of 15 to 22 percent of feedstock which in turn averages 26 to 33 percent of crude charge in Canadian refineries. In other words, light cycle oil yield varies from 4 to 7 percent of crude charge. Virgin middle distillates vary from 26 to 40 percent on crude, depending on the crude with a Canadian average near 30 percent. Thus it is not realistic to plan for a light cycle oil saturation unit the same size as for the other cases. Hence, a 1000 m^3/d nominal size has been selected for analysis.

With light cycle oil there is only very minimal potential to bypass feed and, hence, both NiMo and Ni routes are assumed to achieve 20 percent aromatics in the product.

5.3 FACILITY AND COST BASES

5.3.1 Integration with Existing Facilities

The following assumptions have been made relative to both conventional and nickel based routes with no cost or credit except where noted:

a) Existing Refinery or Upgrading Facility Location in Alberta
b) Land available
c) Services available - laboratory, office, warehouse, maintenance
d) Control Room Personnel - Cnarge project with incremental manpower, spare parts, maintenance materials and other direct costs.
e) Utilities available as needed
   - electricity (at $0.025 per Kwh)
   - nitrogen (for storage and shutdown only)
   - boiler feed water
   - M.P steam (at $9.00 per kg)
   - Sweet Fuel Gas (at $0.053 per m^3 for consumption net of production assuming 0.036 GJ per m^3 HHV).
f) Sulphur handling/recovery facilities available as needed
   - Sour Fuel Gas treating
   - Lean amine (at $5.00 per m^3) at low pressure
   - Rich amine regeneration
   - Sour water stripping facilities
g) Hydrogen available as needed
   - At 2.1 MPa (300 psig) 98 percent purity, trace CO and CO_2 incrementally, at $0.053/$m^3$ - $1.50 per mscfd, from steam methane reforming.
h) Feedstocks
   - at 0.2 MPa and 38°C at battery limit
   - Feedstock and off specification/slop tankage as needed
i) Product systems- Liquid products delivered to battery limits at 0.35 MPa and 43°C to existing tankage.

5.3.2 Capital Costing

Current 1987 Alberta refinery construction costs and independent licensor standards have been assumed. The following chart of accounts and estimating approaches have been used:

Major Equipment	- Preliminary process specifications and internal estimates
Factors to total material	- Varies with case: internal estimates - Differentiated reactors from other equipment
Engineering and related projects overheads	- Internal estimates, includes any assumed royalties
Spare parts	- At 0.6 percent of total materials and labour
Initial Catalyst Charges	- Verbal prices, internal demand estimate
Initial Start-up Costs	- Not included
Interest during construction	- Not included

The approach is estimated to provide capital estimates accurate to about ±35 percent, but more importantly to reflect directional differences (when the differences are more than 15 percent). Note that equipment and piping metallurgy have been selected to match the specific service (102).

No specific contingency is added, as the factors used to extend equipment to material and labour contain allowances for normal contingency items.

5.3.3 Operations Costing

The following approaches and chart of accounts have been used with unit costs as per Section 5.3.1 where applicable. All costs are in current 1987 terms:

Utilities	- Electricity	- Preliminary, estimated by rotating equipment item.
	- Steam	- Stripper steam plus miscellaneous heating preliminary estimates
	- Sweet Fuel Gas	- Preliminary estimate of consumption and of production
Feeds	- Lean amine	- Preliminary estimates
	- Hydrogen	- Preliminary estimates
Catalyst & Chemicals		
	- Catalyst	- Estimates of average annual consumption assuming no regeneration

- Chemicals	- Sulphiding nitrogen and miscellaneous gases and chemicals - preliminary estimates. Amine see above in section 5.3.1.
Maintenance	- 3.5 percent of materials and labour components of capital cost.
Other Labour Costs	- Preliminary estimates of direct labour at $70,000 per man year covering associated overheads, laboratory and operating supplies, etc.
Insurance and Taxes	- 1.5 percent of materials and labour components of capital.

Interest charges on working capital have been neglected as in each pair of comparable cases the difference should be small.

5.4 **CONVENTIONAL ROUTE**

5.4.1 General

Table 5.4.1-1 outlines assumed conditions for an aromatic saturation system using readily available NiMo and NiW catalysts. The following table briefly summarizes the principal process parameters for each of the four feedstocks being considered.

TABLE 5.4.1-1
CONVENTIONAL ROUTE PARAMETERS

Parameter	Units	CASES			
		Suncor Kero	Syncrude MD	Blend(c)	L.C.O.(c)
Feed Rate	m^3/d	2000	2000	2000	1000
Reactor Pressure	MPa	10.1	11.5	13.1	15.2
	(psig)	(1450)	(1650)	(1900)	(2200)
LHSV		2.0	1.5	1.0	0.8
Temperature, Avg.	°C	280	280	315	335
Recycle Gas Rate	m^3/m^3	267	535	535	1070
	(SCFB)	(1500)	(3000)	(3000)	(6000)
Hydrogen Consumption, (b)	m^3/m^3	69	131	150	352
	(SCFB)	(390)	(735)	(840)	(1975)
Catalyst		(a)	(a)	(a)	(a)
Sulphur In/Out	wt ppm	200/<100*	400/<200*	2000/<500	3000/<500
Aromatics In/Out	vol %	30/20	36/20	41/20	70/20

Notes
* Not Controlling
(a) Katalco 506 (NiMo), or Shell 454 (NiW), or equal
(b) Includes losses to fuel gas - very approximate
(c) Feed from mild hydrotreating

The average reactor temperature will vary catalyst to catalyst and with catalyst age as well as feedstock. In practice, the average temperature will rise by 20 to 40°C during the course of a run with the ability to meet aromatic specifications due to equilibrium conditions limiting run length. Different catalysts may require slightly higher temperatures, shortening the run length, but different catalysts will also exhibit different activity decline rates.

The catalyst assumptions are considered representative of the better NiMo aromatic saturation catalysts now on the market. A high denitrogenation capability is also essential due to high portions of cyclic nitrogen to be removed prior to final aromatic saturation in all cases. The Katalco and Shell catalysts were considered in earlier CANMET studies (84)(114), but other vendors have catalysts of very comparable qualities.

In each case, the objectives of the process are to meet a 20 volume percent maximum total aromatics concentration and a 0.05 wt percent sulphur content. The total aromatics target is slightly below an anticipated specification to provide some room for start-ups, shutdowns and process upsets as well as variations in feedstock qualities.

It is to be noted that cetane has not been a specific target in any case (nor has smoke point). In the "blend" case, the resulting cetane number will probably be above 40. However, in synthetic crude derived cases, the use of cetane improver will be needed to bring the cetane number to the 40 level. In the case of light cycle oil, the product will be blended with other stocks of better cetane number in any case. The smoke point of Jet A boiling range fractions of the Suncor and Syncrude products is expected to be acceptable in each case, but the products of the other two cases will not have an equivalent quality.

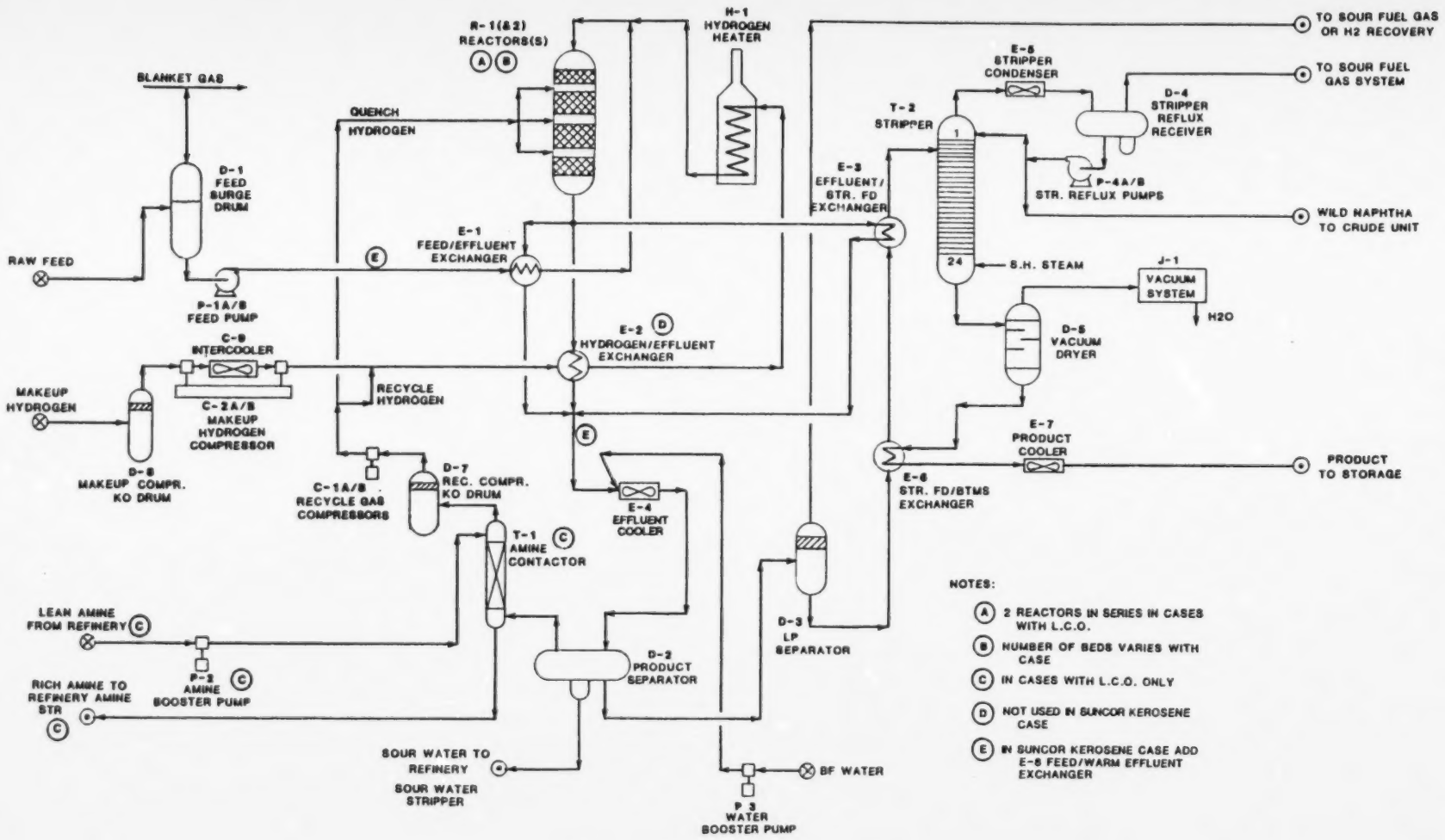
Detailed optimization has not been attempted. A single cold high pressure separator approach has been used, at variance with practice of some companies. The single separator approach provides higher recycle hydrogen purity (92 to 94 percent) and, hence, allows lower design pressures and reduces capital costs slightly. But it does result in a less thermally efficient design and more hydrogen is needed due to higher solution losses.

In practice, some waste heat recovery facilities would be added to those shown to suit local conditions in the light cycle oil only case. A cold feed has been assumed here although a hot feed will be the norm in units not operating in a blocked mode on differing feeds.

5.4.2 Process Description

Figure 5.4.2-1 outlines the anticipated process configuration. In all cases, blanketing of all feedstock storage tanks and related vessels to exclude oxygen will be essential to minimize raw feed exchanger and first reactor bed fouling.

The feed is heated against reactor effluent and then combined with hot hydrogen before entering the reactor (first of two in the last two cases). While the



CONVENTIONAL HYDROTREATER SCHEMATIC

FIGURE 5.4.2-1

temperature levels are relatively mild by hydrotreating standards, in the cases with light cycle oil some attention may be required relative to the potential to fouling of this exchanger even with the pretreated feedstock.

The reactor(s) will be designed with multiple catalyst beds using recycle gas quench between each to provide very close control of the temperature. As the catalyst ages, the pattern of ΔT across each bed will change and the rates of the various quenches will be adjusted accordingly.

The overall reactor temperature rise in the Suncor kerosene case is expected to be about 18°C without any hydrogen interbed quench. This appears well under the assumed maximum of 60°C, but allowance for two beds and an interbed quench has been made in order to control the temperature rise in the top bed with new catalyst and/or during upset conditions. Control of the degree of hydrogenation will require very close attention in all cases. It will be difficult until experience has built up and on line aromatics content analyzers are proven in practice, to keep the outlet aromatics at or near the 20 percent target. There will be a marked tendency to over saturate early in the run; hence, temperature rises higher than necessary for a 20 percent product will often occur.

The distribution of heat of reaction between the various beds will vary with catalyst life and the composition of the feed - total and polynuclear aromatic contents in particular. The latter will tend to saturate first - at least to the monoaromatic level. Hence, there will be more heat evolved in the initial catalyst beds than later ones and bed volumes will be adjusted to suit. This will be particularly true in the case of the feedstocks containing light cycle oil.

The reactor effluent will exchange heat with raw liquid feed, hydrogen and stripper feed before being finally cooled and separated into recycle gas and liquid product. As there will be a tendency to form solid ammonia sulphide deposits in the condenser circuit, a water wash system will be provided for continuous operations in the case of feeds containing light cycle oil and batch washing in the other two cases.

The recycle gas will be scrubbed with amine to remove virtually all contained H_2S before recompression in the two cases with light cycle oil. Due to already low sulphur levels, such scrubbing is not needed in the two synthetic crude derived feedstocks.

The recycle gas rate will be set by heat of reaction removal needs in cases other than kerosene, but the first bed will only see the above noted minimum hydrogen plus makeup rate. As the aromatic and sulphur content of the feedstock will change over time, appreciable flexibility will be essential in the recycle gas compressor in order to have capacity for bed temperature control.

Makeup hydrogen will be brought up to operating pressure in two stages of reciprocating compression. Normal impurities in the makeup - methane, traces of CO and CO_2 - are not expected to cause any problem in this system. The individual compressors will each have 67 percent of full load capacity-

allowing some added capacity in emergency and 2/3 throughout when one is out of service.

The hydrogen heater will be only used for startup in the light cycle oil case, but will be used to trim the temperature of the total reactor charge in the other cases.

The hydrocarbon liquid from the high pressure separator will be flashed in the low pressure separator to eliminate most dissolved hydrogen and light ends to a fuel gas stream, which will require an amine wash to remove H_2S before going to fuel or to hydrogen recovery.

The liquid from the low pressure separator will be heated in two stages before entering the stripper. A small amount of steam will strip the C_8 minus components from the product to meet flash point and H_2S specifications. The stripper bottom will be dehydrated in a vacuum drier system to provide a haze free product.

5.4.3 Special Operations

During startup and shutdown the product will be recycled to the feed surge drum or feed storage tank.

New and regenerated catalyst will require presulphiding. Suitable catalyst is now available from one vendor in a factory presulphided form and this may well prove to be the optimum route, especially due to the gains in on stream time. However, the unit will be provided with presulphiding facilities, in any case. Economics of the day will determine whether catalyst will be discarded after every run or regenerated. Due to environmental and catalyst activity concerns, when used, offsite regeneration is now the norm.

Herein it is assumed that in cases with light cycle oil, 25 percent of the catalyst is replaced with fresh catalyst every 10 months and the other 75 percent is replaced every 18 months. In the other cases, total replacement with fresh catalyst every 18 months has been assumed.

The recycle gas compressors will be the key pieces of process equipment, as any loss of hydrogen circulation could well result in a temperature runaway in the reactor due to uncontrolled aromatic saturation. If electricity is unreliable at a particular site, a steam turbine drive will be essential for one of the recycle compressors.

5.4.4 Stream Factor

The availability of a conventional NiMo/saturation unit as described here will be in the order of 96 percent, exclusive of planned shutdowns and any major electrical outages.

5.5 NICKEL SATURATION ROUTE

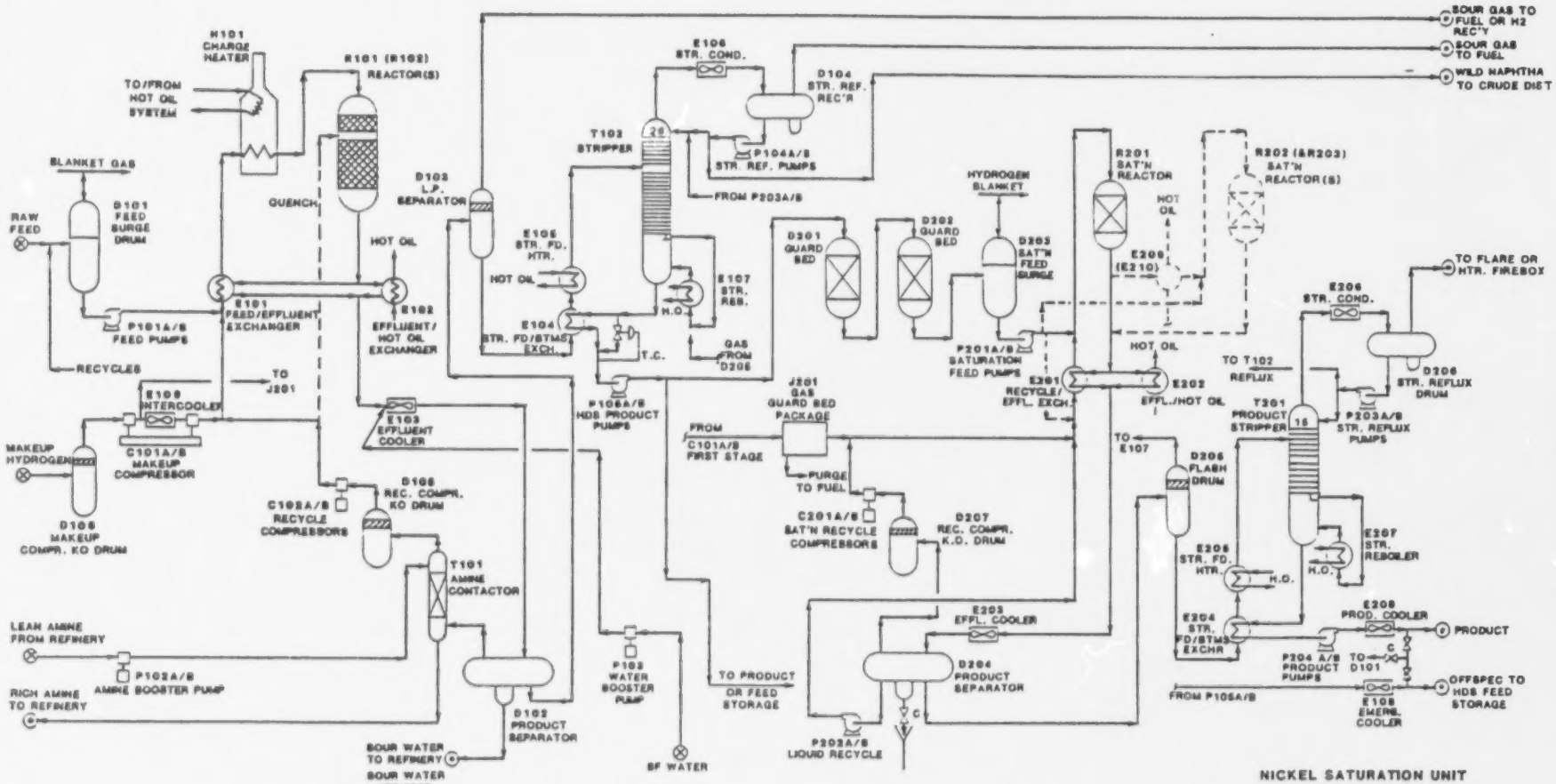
5.5.1 Process Parameters

Figure 5.5-1 outlines a concept for a desulphurization/aromatic saturation system using a nickel based saturation catalyst (116)(117). The following table briefly summarizes the principal process parameters for each of the four feedstocks being considered and each of the two principal process stages:

TABLE 5.5-1
NICKEL ROUTE PARAMETERS

Parameter	Units	Suncor Kero		Syncrude MD		Blend		L.C.O.	
		HDS	Ni	HDS	Ni	HDS	Ni	HDS	Ni
Overall Feed Rate	m^3/sd	2000		2000		2000		1000	
Unit Feed Rate	m^3/sd	800(a)	800(a)	1100(a)	1100(a)	2000	2000*	1000	1000*
Pressure	MPa (psig)	8.4 (1200)	3.2 (440)	10.5 (1500)	4.2 (600)	10.5 (1500)	4.2 (600)	10.5 (1500)	4.2 (600)
LHSV		2.0	4.0	1.5	3.0	1.2	3.0	0.8	1.5
No. of Reactors		1	1	1	2	1 or 2	2	2	3
Reactor Temperature									
SOR	°C	349	160	354	170	354	170	354	170
EOR	°C	360	250	366	250	366	250	366	250
Recycle H_2	m^3/m^3 (SCFB)	178 (1000)	356 (2000)	178 (1000)	445 (2500)	178 (1000)	445 (2500)	267 (1500)	980 (5500)
Liquid Recycle to Product	m^3/m^3 feed	--	approx 1/1	--	<1/1	--	<1/1	--	<1/1
Total Hydrogen Makeup	m^3/m^3 of Overall Feed (SCFB)	61 (343)		146 (820)		164 (920)		352 (1980)	
Catalyst		(b) --	-- (c)	(b) --	-- (c)	(b) --	-- (c)	(b) --	-- (c)
Sulphur In/Out	ppm	200/<5	<5/0	400/<5	<5/0	2000/<5	<5/0	3000/<5	<5/0
Aromatics									
In	vol %	30	--	36	--	41	--	70	--
Out	vol %	--	5	--	<5	--	20	--	20

Note: * may be lower in practice due to ability to bypass small portion of product around saturation stage
(a) Rest of overall feed bypassed directly to product.
(b) CoMo on alumina - Akzo 742, UOP S12 or equal
(c) Harshaw Ni 3288 or equal, Nickel on silica alumina
(d) Some PNA saturation likely but total aromatics unlikely to change.
(e) Very approximate



NICKEL SATURATION UNIT SCHEMATIC

FIGURE 5.6-1

Hydrogenolysis and hydrocracking considerations will probably set the upper limit on saturation reactor temperature; the upper limit shown here is to some extent arbitrary but no impact on aromatic saturation is expected with the nickel catalyst unless below 2 or 3 volume percent aromatics is desired. In the last three cases, multiple reactors are used for saturation and the temperatures will be set individually.

The catalyst assumptions are considered representative of the better catalysts available for the specific functions at this time. The nickel catalyst selection is a higher nickel content, more active catalyst than that tested by CANMET (114). It is also slightly more sulphur resistant.

Due to the very low sulphur tolerance of the nickel catalyst the hydrodesulphurization portion of the facility will be operating at severities well beyond those in normal refinery middle distillate hydrotreating. Only solvent kerosene and white oil production - very specialized operations - come close, although desulphurization of naphtha before catalytic reforming regularly achieves levels of less than 0.5 ppm sulphur in the product with a much lighter feed.

Liquid product recycle is assumed in order to control the temperature rise across the first reactor and to provide good temperature control inside the individual catalyst beds. The operating pressure for the nickel saturation system has been set above that recommended by CANMET for the more aromatic feeds to provide better local reactor temperature control and to better saturate the trace of olefins in the feedstock arising from HDS reactions. Further testing may show lower pressures are quite satisfactory.

5.5.2 Guard Beds

The economic sulphur levels are at the <1 ppm level relative to the saturation catalyst. At least two catalytic reforming process licensors very strongly recommend guard beds before their platinum/rhenium catalysts to remove the last traces of sulphur (58). One middle distillate process licensor also suggested their use here. The use of such guard beds are proposed to maximize saturation catalyst activity and its life. At this time, no final selection of guard bed material has been made. but a nickel material has been assumed. The activity of the guard bed adsorbents towards thiophenic sulphur appears good (due to proven usage in reformers), but further testing is needed to confirm this in middle distillate service.

Guard beds will operate at 160 to 220°C in the liquid phase with no hydrogen present. The nickel adsorbent adsorbents available all have some aromatic saturation capability in a hydrogen rich atmosphere, but it was judged more economical to use them strictly as sulphur adsorbents. No known organic nitrogen adsorbents have been identified.

The level of sulphur in the HDS stage product is very important to the overall process - a high level simplifies HDS design, lowers costs and reduces operation control needs but at the expense of increased guard bed adsorbent costs, a major operating cost factor. There is appreciable evidence to indicate that even at 100 percent desulphurization the "equilibrium" sulphur at

the outlet of the HDS stage will be in the order of 1 to 2 ppm due to reaction of traces of olefins with hydrogen sulphide at the outlet of the last catalyst bed (58). It is expected that there will be a minimum of total sulphur in the HDS effluent at given temperature, unconverted sulphur increasing below that point and recombined sulphur increasing above. For this report a 5 ppm sulphur level in the HDS product has been assumed - 2 ppm for recombination and 3 ppm for unreacted thiophenic type sulphur.

The saturation catalyst itself can act as a sulphur absorber but does not achieve the essentially 100 percent removal up to a breakthrough point as do the adsorbents noted above. Spent catalyst nevertheless provides potential for reduction of adsorbent needs. For this study the following plan was assumed:

Guard Beds
- Provide 2 vessels in series each sized to match the size of individual saturation reactors.
- Initially charge second vessel with selected adsorbent. (This will give 7 to 11 months life at 5 ppm in and 0.5 ppm out.)
- When spent saturation catalyst is available, place in first guard bed.
- On each saturation catalyst change, replace first guard bed material, sending that previously there to catalyst disposal service.
- Replace final guard bed adsorbent at first indication of breakthrough.

Saturation Reactors
- When the first reactor activity declines below acceptable limits, move catalyst forward with first reactor material going to first guard bed as above, or to metal recovery if not needed in guard bed. This may be done by changing the position of the particular reactor in the process flow - the last reactor will always have the fresh catalyst.

Such a scheme should provide about two year life on the average for the guard bed adsorbent and one year plus for the saturation catalyst.

5.5.3 Saturation Catalyst

At this time this study has not identified any nickel saturation catalyst with significant sulphur resistance. The preliminary calculations of this study assumed a one year life due to sulphur poisoning - at a final activity approximately 50 percent of initial. However, the high HDS temperature may result in traces of olefins causing "coke" deposits shortening this life.

It is possible to remove that "coke" through complex regeneration schemes involving controlled oxidation. However, no proven approaches for the removal of adsorbed sulphur applicable to commercial operations were noted.

The selected catalyst is available in a reduced form with a monomolecular layer of carbon dioxide for safety in handling ("stabilized"). An activation step is needed to remove the CO_2 layer when the catalyst is first charged. This

involves slowly raising the temperature in a nitrogen atmosphere and then displacing the nitrogen slowly with hydrogen. After this activation procedure it is recommended practice to run with diluted feed - i.e. low aromatic content - for another 24 hours. Overall, two days appear minimum to bring on a new catalyst bed.

When reactors are to be opened to the atmosphere, special precautions are needed unless the catalyst has been "stabilized" in a manner similar to that at the factory.

Appendix A discusses safety, hygiene and environmental control when using nickel catalysts.

5.5.4 Objective Achievement

The primary objective of the system is to lower the aromatic content of the overall feed in each case to 20 volume percent or lower to meet current jet fuel and possibly future diesel fuel aromatic standards. A parallel objective will be to achieve a sulphur content below 0.05 weight percent in the total feed. The latter necessitates full feed processing in the blend and light cycle oil cases, at least through the HDS section.

The table above notes the design feed rates for the four cases. There will be some saturation in the hydrodesulphurization section, although the high temperature makes equilibrium consideration more important than kinetics, greatly limiting saturation. Generally, literature data show little or no improvement in total aromatics from a volume percent standpoint, but do show significant reduction in polynuclear aromatics through conversion to mono-aromatics - in the order of 30 to 40 percent (121). Thus some credit is necessary to allow for the reduced load on the saturation unit with part of the hydrogen consumption moved to the HDS unit.

As there may be some reduction in the volume of total aromatics due to the HDS operation, some bypassing of HDS product around the saturation unit may prove possible in practice. The schematic diagram - Figure 5.5.5-1 of the next page - shows such a capability. The only benefit of aromatic saturation in the HDS unit assumed herein has been in a lower heat rise in the saturation reactors, allowing a slightly lower liquid recycle rate, particularly in the light cycle oil case.

With the liquid recycle of the proposed nickel catalyst saturation systems, a very high percentage of polynuclear aromatic compounds will be converted to monoaromatics and partly, thence, to saturated compounds. The remaining aromatics will be predominantly monoaromatics even in the light cycle oil case.

It is to be noted that this nickel saturation route will not raise cetane numbers of the various feeds to the 40 specification level except in the blend case. Bypassing of feedstock around the saturation system in the Suncor kerosene and Syncrude middle distillate cases may result in more PNA's in the product from nickel saturation than in (full feed) conventional NiMo processing and, hence, a slightly lower cetane number and smoke point. This may require less bypassing to bring the nickel route product to the same levels as that of

the NiMo route, but it is believed that such added processing can be accomplished in the system as estimated here. In all cases, some added aromatic reduction has been assumed to be required for unit design to meet product aromatic specifications on a consistent basis than for specification achievement during normal operation.

5.5.5 Process Design

5.5.1 Hydrodesulphurization

This portion of the system is very similar to conventional systems differing primarily in space velocity and the high reactor temperature required to achieve a very high degree of desulphurization. Temperature is generally more important in desulphurization than catalyst volume.

Normally pressure is not very important in desulphurization but the extremely tight product specifications require a much above normal pressure. Indeed, the pressures assumed here are above all present Canadian middle distillate hydrotreaters except those at Syncrude, Suncor and Petro-Canada in Edmonton. In further work relative to development of the HDS/nickel route detailed investigation of the appropriate HDS temperatures, pressure and catalysts will be essential.

Again a single cold separator approach has been assumed for the HDS system to simplify operations and reduce capital as well as maximize hydrogen partial pressure. The feed will be blended with hydrogen recycle before exchange with reactor effluent. This exchanger will present some challenge particularly in the light cycle oil case in minimizing fouling due to the high reactor effluent temperatures. Antifoulant chemicals may be used. The charge heater which follows does not present the same challenge due to the ability to easily decoke it during shutdowns.

The HDS reactors in the cases with light cycle oil will have two beds, each with the ability to quench with hydrogen between beds and between reactors if temperatures rise unduly due to PNA saturation. The other two cases will have single reactors and one interstage quench for emergency use. The top catalyst bed in the lead reactor in light cycle oil cases will be subject to coking and frequent - say every 10 to 12 months - change is foreseen. (This would ideally occur when saturation catalyst is changed in the other portion of the unit.) Both Suncor and Syncrude stocks will have been hydroprocessed under even more severe conditions and are viewed as very clean feeds.

A water wash system is provided to wash salts out of the reactor effluent system. In all cases recycled gas will be thoroughly scrubbed with amine to remove H_2S although about half of the H_2S formed will leave with the liquid from the product separator.

The liquid product will be flashed to remove dissolved hydrogen and some light ends and then thoroughly stripped to remove all H_2S. The gasoline boiling range decomposition products will be sent to the crude unit.

5.5.5.2 Saturation Section

The liquid product from the HDS section, at about 175°C, will flow through the two guard beds in series to remove virtually all residual sulphur compounds.

Due to the warm feed and expected low reactor temperatures - in 160 to 230°C range - feed will not normally be heated but will join heated hydrogen and recycle liquid before going to the reactor. Reactor temperature rise control is via recycle, in all cases. Gas quench could be used here but the normal benzene hydrogenation approach of liquid recycle is considered more appropriate for the high activity nickel catalyst.

In the multi reactor cases - two for Syncrude middle distillate and blend and three for light cycle oil - the feed is split between reactors to minimize temperature rise and aromatics concentration at any one point. This results in a large surplus of hydrogen at all points, but lower recycle/feed ratio in the first reactor and the converse in the last reactor, compared with the single reactor case. In practice, the feed split will be adjusted to reflect individual reactor catalyst activities. The lead reactor will be the least active, with its liquid product passing through the remaining reactors where final aromatic reduction is achieved; thus it will probably get a larger than equal portion of the feed.

The liquid from the product separator will contain dissolved hydrogen and a trace of light end decomposition products to be removed in a flash and stripping system.

In order to keep the purity of the hydrogen at the high level required for the nickel catalyst, a molecular sieve, or equal, guard bed system is proposed to remove any traces of H_2S and/or carbon oxides from the makeup hydrogen. In furtner design, an H_2S adsorber in the total hydrogen flow should also be considered to guard against upsets and further protect the saturation catalyst. Such has been used before in benzene hydrogenation using zinc oxide as adsorbent. All compressors will be reciprocating with each rated at 67 percent of full load capacity, allowing some flexibility in operation and 67 percent throughout with one out for service.

The liquid recycle is essential to temperate control and it is expected that the spare recycle pump will have a steam turbine drive that kicks in on power failure. On power failure, cold liquid recycle will flow to each reactor to cool it down and avoid potential hydrocracking conditions.

5.5.5.3 Heat Recovery

The schematic indicates a hot oil system to provide heat for stripper reboilers and stripper feed heaters. Use of hot oil in these cases provides a buffer between high H_2S content streams and streams requiring essentially no sulphur.

But there will still be a surplus of heat in the 100 to 150°C range available for off plot uses. Here, the hot oil system is assured to transfer excess heat to the atmosphere; in practice some economically viable use of that energy is very likely to evolve. The hot oil system will probably consist of two loops-

a high temperature one to provide heat to reboilers and stripper feed heaters and a low temperature circuit to remove surplus heat.

5.5.6 Stream Factor

The following availabilities are estimated, exclusive of planned shutdowns and externally caused slow ups and/or shutdowns:

- Suncor Kerosene 96%
- Syncrude Middle Distillate 95%
- Blend 95%
- Light cycle oil 94%

The reducing availabilities are due to added catalyst change outs in the more severe cases. During such periods only partial throughput will be possible.

5.6 YIELD DATA

The following table summarizes estimates of yields for the various cases for "normal" operation scenarios. The hydrogen consumption is related to "design" conditions and in practice the quantities will likely be less.

TABLE 5.6-1
YIELD AND UTILITY CONSUMPTION DATA

		CONVENTIONAL NiMo HDS				NICKEL AROMATIC SATURATION			
Stream	Units	Suncor Kerosene	Syncrude Mid Dist	Blend	L.C.O.	Suncor Kerosene	Syncrude Mid Dist	Blend	L.C.O.
Feedstocks									
Overall Feed	m^3/d	2000	2000	2000	1000	2000	2000	2000	1000
Net to Processing	m^3/d	2000	2000	2000	1000	800	1100	2000	1000
Hydrogen Makeup	$10^3m^3/d$	139	263	300	352	125	292	329	354
Products									
Mid Distillate	m^3/d	2014	2024	2012	1031	2015	2026	2010	1028
Naphtha	m^3/d	16	34	40	35	14	34	60	45
Fuel Gas	(MMBTU/hr)	8.5	14.0	17.0	16	5	12	22	12.5

The above data indicate very little difference between the alternate routes relative to yields.

5.7 CAPITAL COSTS

5.7.1 Comparison

The following table summarizes the preliminary capital cost estimates for the alternate cases:

TABLE 5.7.1-1
CAPITAL COST ESTIMATES
- in Millions of '87 Cdn Dollars -

Account	Conventional NiMo Cases				Nickel Cases			
	Suncor Kerosene	Syncrude Mid Dist	Blend	L.C.O.	Suncor Kerosene	Syncrude Mid Dist	Blend	L.C.O.
Material, Plus Labour	17.3	20.5	25.5	25.5	17.7	22.1	29.0	27.3
Engrg. & Related Costs	2.6	3.0	3.3	3.5	3.2	3.4	3.6	3.6
Spare Parts	0.1	0.2	0.2	0.2	0.2	0.2	0.2	0.2
Catalysts	0.3	0.3	0.5	0.3	0.5	0.8	1.5	1.3
TOTAL COST	20.3	24.0	29.5	29.5	21.6	26.5	34.3	32.4

An allowance for royalties has been included in the "Engineering and Related Costs" account. The accuracy of the overall estimates is in the order of ±35 percent. The difference between alternates should be at least 15 percent to be significant.

5.7.2 Platinum Based Reference Point

UOP has provided preliminary estimate for two sizes of light cycle oil AH Unibon two stage units as follows:

5000 BPSD $23.6 million US ('87 US Gulf Coast)
2000 BPSD $12.7 million US ('87 US Gulf Coast)

The light cycle oil of these cases is similar to that assumed in this study but UOP started with about 1.7 weight percent sulphur versus 0.3 here (51).

With the Canadian dollar assumed worth $0.75 US and allowing a 10 percent location penalty, a 1000 m3/d AH Unibon unit, complete with catalyst, will cost approximately $32 million Canadian.

While UOP's and RTM's estimating approaches and facility coverage vary, this figure is suitable for early process screening purposes for UOP's platinum based approach. It is to be noted that the large majority of the catalyst costs are related to platinum which is recoverable at over 90 percent yield from spent catalyst. A six year life is estimated for the platinum saturation catalyst. While no detailed operating cost comparison has been prepared, they should be similar to or slightly less than for a Ni route due to lower catalyst costs.

5.8 OPERATING COSTS

The following table summarizes the preliminary operating cost estimate for the alternate cases:

TABLE 5.8-1
OPERATING COST ESTIMATES
in Millions of '87 Cdn Dollars per Year

Account	Conventional NiMo Cases				Nickel Cases			
	Suncor Kerosene	Syncrude Mid Dist.	Blend	L.C.O.	Suncor Kerosene	Syncrude Mid Dist.	Blend	L.C.O.
Fuel (Net of Prod.)(a)	0.0	-0.1	-0.1	-0.2	0.2	0.2	0.5	0.2
Electricity	0.2	0.3	0.4	0.5	0.1	0.3	0.4	0.4
Otner Utilities	0.2	0.2	0.2	0.1	0.1	0.1	0.1	0.1
Catalyst & Chemicals(b)	0.2	0.2	0.4	0.3	0.4	0.7	1.3	1.2
Maintenance	0.5	0.7	0.9	0.9	0.6	0.8	1.0	1.0
Operating Labour & Overhead	0.2	0.2	0.2	0.2	0.4	0.4	0.4	0.4
Insurance and Taxes	0.3	0.3	0.4	0.4	0.3	0.3	0.4	0.4
SUBTOTAL	1.7	1.8	2.4	2.3	2.1	2.7	4.1	3.2
Hydrogen	2.4	4.6	5.2	6.1	2.2	5.1	5.7	6.2

Notes
(a) Produced gas as shown in table 5.6-1 is assumed used onsite first (although it must be treated off plot to remove sulphur before any use).
(b) In the above, spent catalyst and adsorbent are assumed returned to the vendor at no cost or credit.)

The hydrogen cost shown is for "design feedstock product. In all cases except light cycle oil, the average hydrogen consumption will be less by 20 to 30 percent with "better" feed and slightly more aromatics in the product (closer to actual prevailing specification).

The accuracy of these costs is in the order of ±30 percent and differences between alternates need to be approximately 15 percent to be meaningful. A bias towards higher costs for the nickel route is indicated, when hydrogen is taken out for all but the light cycle oil cases.

5.9 COMPARISON SUMMARY

The following table summarizes the comparison study between NiMo and Ni catalyst routes to middle distillate saturation.

TABLE 5.9-1
COMPARISON

Factor	Suncor Kerosene		Syncrude M.D.		Blend		Lt. Cycle Oil	
	NiMo	Ni	NiMo	Ni	NiMo	Ni	NiMo	Ni
Yields								
Mid Distillate m3/d	2024	2015	2024	2026	2012	2010	1031	1028
Naphtha m3/d	16	14	34	34	40	60	35	45
Capital Costs	20.3	21.6	24.0	26.5	29.5	34.3	29.5	32.4
$MM Cdn '87								
Operating Costs								
$/m3 product	2.60	3.20	2.70	4.10	3.65	6.2	7.00	11.20
$/bbl product	0.41	0.50	0.43	0.65	0.58	0.0	1.11	1.78

5.10 SATURATION ONLY

5.10.1 Preamble

In sections 2.7.2 and 2.7.3 above, some potential for saturation systems without prior HDS is indicated. This will occur in instances where existing hydrotreaters can provide a feed with sulphur content below roughly 15 ppm and nitrogen content is 1 ppm or less. Hydrocracker kerosene can also be considered where the nitrogen is sufficiently low - 1 ppm or less.

5.10.2 Capital Cost

The following table breaks out the HDS and nickel saturation system costs for the four feedstocks. Engineering and related costs have been arbitrarily split between the systems.

TABLE 5.10.2-1
NICKEL ROUTE CAPITAL COST BREAKDOWN
in Millions of '87 Canadian Dollars

Account	Suncor Kerosene		Syncrude Mid Distillate		Blend		Lt. Cycle Oil	
	HDS	Ni	HDS	Ni	HDS	Ni	HDS	Ni
Material plus Labour	13.2	4.50	15.9	6.20	21.1	7.9	19.8	7.5
Engrg. & Related	2.3	0.90	2.4	1.00	2.6	1.0	2.6	1.0
Spare Parts	0.15	0.05	0.15	0.05	0.15	0.05	0.15	0.05
Catalysts	0.10	0.40	0.20	0.60	0.40	1.10	0.30	1.00
SYSTEM TOTAL	15.75	5.85	18.65	8.85	24.26	10.05	22.85	9.55
CASE TOTAL	21.6		26.5		34.3		32.4	

Note: The accuracy of individual datum noted above and the system totals may be less than the Case Total figure. Due to rounding some figures may not total precisely.

5.10.3 Operating Cost Breakout

Table 5.10.3-1 below presents an approximate breakdown of the operating costs presented previously in section 5.8-1. Hydrogen is kept separate as it will vary with the degree of saturation needed but other costs will be essentially constant regardless of feedstock or product aromatic level.

TABLE 5.10.3-1
NICKEL ROUTE OPERATING COST
- in millions of '87 Cdn dollars per year -
- exclusive of hydrogen makeup -

	Suncor Kerosene	Syncrude Mid. Dist.	Blend	Light Cycle Oil
HDS	1.2	1.45	1.8	1.75
Saturation	0.9	1.25	2.3	1.95
TOTAL	2.1	2.7	4.1	3.7

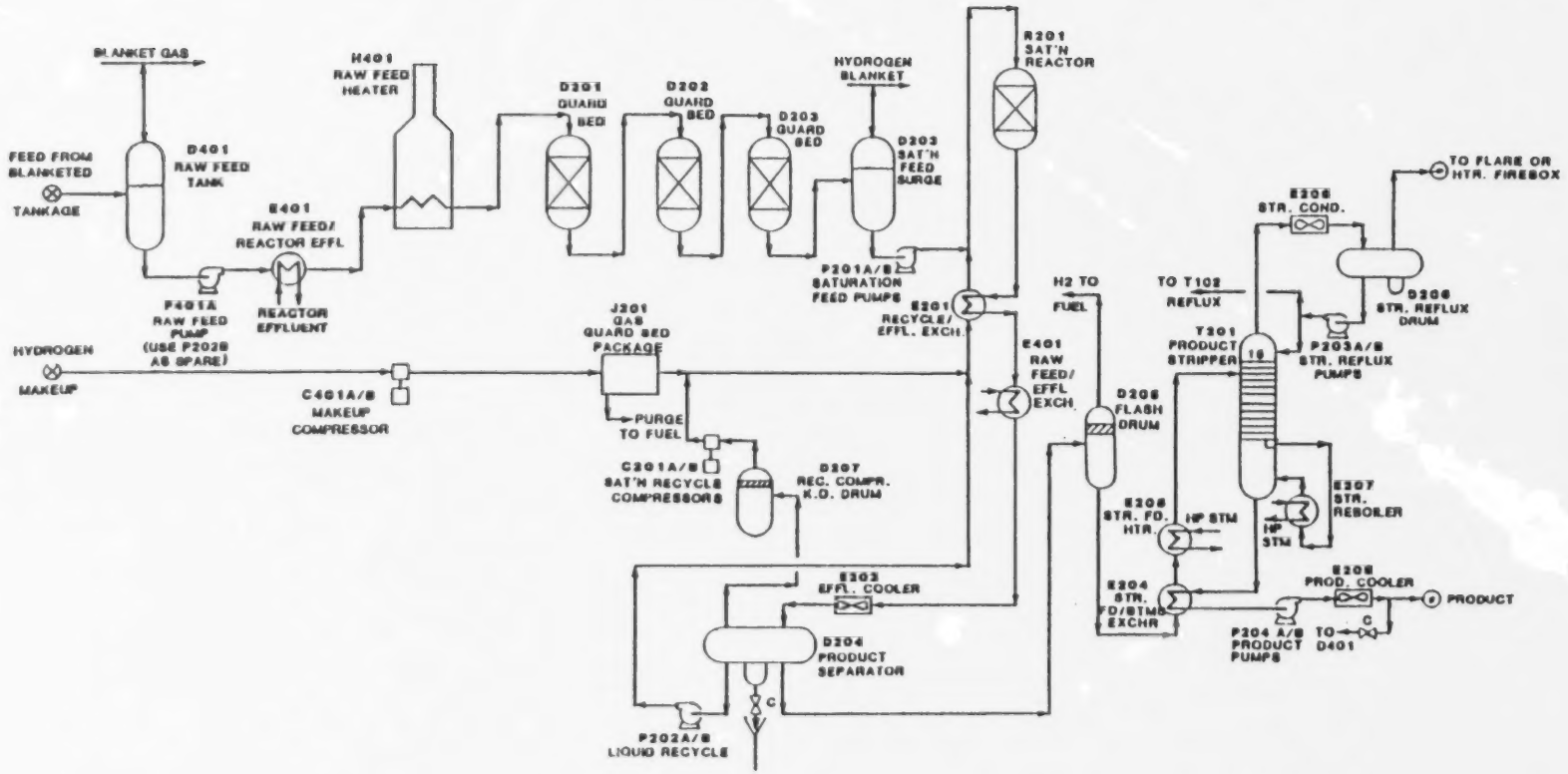
The majority of Ni route operating cost - other than for hydrogen - is for saturation catalyst and guard bed adsorbent. Other costs are in about two thirds relative to the HDS portion of the facility.

5.10.4 Stand Alone Saturation Unit

Figure 5.10.4-1 outlines the concepts of a stand alone saturation unit processing a kerosene boiling range feedstock, with 5 ppm of sulphur and 1 ppm or less of nitrogen, to a low - <5 percent - aromatic content product. An 800 m^3 per day saturation unit is assumed, equivalent to 2000 m^3 per day of total feed average 30 volume percent aromatics and a 20 volume percent specification.

High pressure steam has been assumed available from adjacent facilities for stripping heat needs as unfortunately the excess heat of reaction goes to feed and recycle heating and is at too low a level to be of use for reboiling. A fired heater has been added to heat cold feed to the guard beds as the water tolerance of the nickel catalyst has been assumed low and a steam heater might leak on occasion. In practice, hot oil might be used for feed and stripping heat. With a higher boiling range feed, live steam stripping would probably be used.

A third guard bed has been added to those assumed in above cases with prior HDS. Initially two would be charged with adsorbent, but eventually the first two would be on spent saturation catalyst. Here, replacement of the adsorbent every nine months has been assumed. This should be satisfactory at the 10 to 15 ppm level assuming tests on actual feedstock confirm essentially 100 percent sulphur capture.



STAND ALONE SATURATION SYSTEM

FIGURE 5.10-4-1

Capital costs increase over the Suncor kerosene case will arise due to added feed pump and drum, added guard bed, changes in compressor packaging, and added engineering and related costs due to the "stand alone" nature of the unit.

Table 5.10.4-1 summarizes a preliminary estimate of capital and operation costs for an 800 m^3/d kerosene treating unit able to reduce 2000 m^3/d of total feed from 30 to 20 percent aromatics.

TABLE 5.10.4-1
SINGLE STAGE NICKEL SATURATION UNIT COSTS
- in Millions of '87 Cdn Dollars -
- at 5 ppm S in feed -

CAPITAL - Materials and Labour	8.0
- Engineering and Related	1.2
- Spare Parts	0.1
- Catalyst and Adsorbent	0.7
TOTAL	$10.0
ANNUAL OPERATING - Catalysts	0.4
- Other	1.0
Subtotal	1.4
- Hydrogen	2.0

Exclusive of hydrogen, the operating cost per cubic meter is projected in the order of $2.10 ($0.37/bbl) for 2000 m^3 of 30 percent aromatic feed reduced to 20 percent aromatics. Hydrogen costs need to be added to the above at approximately $3.00 per m^3. The yield of kerosene saturated to the 3 to 5 volume percent level is estimated at 102 percent or about 101 percent when saturated to the 20 percent level.

Economics appear best for bypass cases with a small volume processed at high saturation levels than for larger volumes at low saturation levels as most capital and operating costs are dependent on throughput and not the degree of saturation.

Increasing the sulphur level to 15 ppm will add operating costs of about $630,000 per year - equal to about $0.96 per m^3 of total feed ($0.15 per barrel) assuming 2000 m^3 of total feed and 800 m^3 to saturation. Such a cost increase would appear justified if the alternate is hydrodesulphurization of the feed as in the Unisar process. However, conventional platinum catalyst may be preferred due to its higher sulphur tolerance and ease of regeneration over the 3 to 5 ppm range.

5.11 NICKEL CATALYSTS INDUSTRY

Currently, there is no nickel catalyst produced in Canada but it appears very likely that each of the three existing Canadian hydrotreating catalyst manufacturing plants could be adapted at little cost to the production of a

high nickel catalyst such as considered here (57). In comparison with the conventional hydrotreating catalyst industry, the addition of a major market for such a catalyst should also lead to major reduction in the cost of such a catalyst, possibly by as much as 50 percent. Such a reduction would lower capital and operating cost of a nickel based approach significantly.

Guard bed material manufacture has not been considered but again a higher demand should bring the price down and local manufacture might be anticipated.

Higher volume sales of nickel catalysts will also lead to nickel reclamation facilities much closer than those of the southern U.S. This will lead to a minor credit for spent catalyst, but such credit is not expected to significantly contribute to overall process economics. Return of spent nickel catalyst to the original vendor is expected to be the norm with any credit/debit for reprocessing included in his original charge.

The above assumes that the developer of a new nickel process route and/or the respective catalyst manufacturer will provide the same high level of technical support now available from other process licensors and catalyst vendors for competing processes and catalysts. The major cost of such technical support and of ongoing product/application development is to be noted.

6. CONCLUSIONS

6.1 CANADIAN REFINER NEEDS

Currently refiners appear in reasonable shape relative to both Jet A and diesel fuel qualities and volumes. There is some room for added Jet A from conventional crudes but smoke point and aromatic qualities constrain S.C.O. use for Jet A at all but one S.C.O using refinery. Low cetane in diesel fractions from S.C.O. is now balanced by cetane improver use and selective middle distillate product blending.

Use of hydrocracked kerosene for Jet A production may become necessary in refineries now using S.C.O. but not having an aromatic saturation unit as at Shell Scotford. Such kerosene may be too high in aromatics for inclusion in Jet A. Some tightening of the aromatic content specifications of Jet A are anticipated.

The major increase in cost needed to allow future aromatic saturation (NiMo) or very deep desulphurization (before Ni or Pt saturation) will preclude pre-expenditures for undefined future saturation needs.

In the longer term, higher S.C.O. production, introduction into western Canada of Beaufort Sea crude, and declining conventional light crude qualities will create challenges in western Canada and Ontario relative to Jet A quality-smoke point and aromatics - and to minimizing middle distillate production especially in Ontario. As Syncrude is increasing its cetane and new upgraders will produce a 40 cetane product, the cetane problem may not be a major constraint -but the degree of improvement in the long term is now undefined.

The odds are 50 percent or less that an aromatic specification will be put on Canadian highway diesel fuel by about 1996. But higher odds appear likely that reduced sulphur standards will be introduced in the early 1990's for all middle distillates. The latter will result in many new desulphurizers, which will not reduce the total volume of aromatics but which will convert part of the polynuclear aromatic content to monoaromatics. This will marginally improve cetane number and smoke point, where applicable, at the refinery level.

In the short term, up to four kerosene saturation units may be considered, and possibly four or five diesel saturation units in the long run (1995 on). However, the odds appear to be only about 50 percent that the latter will be needed due to a new diesel fuel aromatic content specification.

In the short term, it appears that the main refinery interest will be in Jet A quality improvement - diesel fuel aromatics are unlikely to be of significant interest until 1992, or so, and then only if cetane improver use is ruled out or a diesel aromatic specification appears much more likely than now. It appears that new hydrodesulphurizers will be built for that purpose only, with the exception of a few situations where a small amount of saturation will improve kerosene quality sufficiently for use in Jet A.

6.2 NICKEL CATALYST COMPETITIVENESS

Currently available nickel catalysts appear competitive for aromatic saturation with platinum when feedstock nitrogen is below 1 and sulphur is below about 5 ppm, and they may be, in certain circumstances, competitive when sulphur is over about 5000 ppm when HDS capability is needed in all routes. In all the above applications with the supported nickel, when the feestock sulphur is above about 1 ppm, guard beds of a sulphur adsorbent are required due to the very low tolerance of the nickel catalyst. Between about 5 and 15 ppm of sulphur with enhanced guard beds, nickel catalyst may be competitive with platinum but this study has not examined this relationship. (Unocal's Unisar PtS route appears likely to be preferred in the 15 to 500 range due to the lower integrated desulphurizing capital costs compared with a separate desulphurization facility needed by nickel and other platinum catalysts.)

All hydrogen addition routes are very capital intensive, especially above 10 to 20 ppm of sulphur, with about 75 percent of the capital cost for Pt and Ni routes being in desulphurizing.

Demonstration of the ability to hydrodesulphurize to the 1 to 5 ppm level with full boiling range diesels using CoMo or equal catalysts is needed. There are also needs to define the nitrogen tolerance of nickel catalysts - a level of 3 to 5 ppm could change the competitive picture from the 1 ppm assumed here. But new platinum catalysts able to handle up to 150 ppm of sulphur and possibly 3 or more ppm of nitrogen need watching. They will tend to displace the Unocal Unisar process between 20 and 150 ppm of sulphur and not directly impact on nickel catalysts, except in high nitrogen situations (such as hydrocracked products). The nickel catalyst route with its minimal sulphur and nitrogen tolerances is seen as competitive in certain situations, but without major cost advantages compared to other routes. The current inability to regenerate the nickel catalyst will prove a major impediment to market penetration. There may be new competition in new formulations and catalysts now used only in petrochemical processing. Due to the high costs involved, refiners will look at other alternates to these hydrogenation routes for at least Jet A improvement. For at least Jet A extraction may be a viable alternate (108). Catalyst developers are very active in all areas of middle distillate processing and better catalysts can be anticipated.

6.3 NEW DATA NEEDS

The data used in this study relative to the nickel route need confirmation in many cases. Further data will be required for industry acceptance of the process. The following is a brief listing of specific needs.

a. Aromatics

Industry wide protocols on aromatics testing in general and on nomenclature are urgently needed.

b. Correlations

Smoke point and luminometer numbers for jet fuel need to be relatable to the hydrocarbon types present in kerosene boiling range materials. Cetane number and, in particular, diesel emissions need further development work in the same regard.

c. Hydrodesulphurizaton/Hydrodenitrogenation

Pilot and commercial testing of various hydrotreating catalysts on typical feedstocks down to the 1 ppm level of both sulphur and nitrogen as required by the current nickel catalysts, are essential to optimize this portion of the system.

d. Guard Bed Adsorbents

Detailed tests on breakthrough curves for alternate materials are needed relative to the sulphur compounds present in diesel boiling range materials.

e. Nickel Catalyst Data

Life tests and trace impurity impact test data are required. Hydrogenation routes and kinetics for all aromatic types need to be developed for various operating conditions and variations by molecular weight for individual types need to be defined. Testing regarding safe operating ranges is also needed.

7. RECOMMENDATIONS

7.1 GENERAL

Significant background work is needed to interface with refinery short term Jet A interests and longer term diesel emission concerns, as well as current research and development elsewhere in both areas. Much of the work needed in these areas follows items discussed in (a) and (b) of subsection 6.4 above.

CANMET already has work underway relative to "aromatics" testing procedures which may prove a very useful contribution in that difficult area.

The following sections outline recommended future development activities.

7.2 COMPETITIVE ROUTES

(a) Fundamental work on cetane improving chemicals may prove worthwhile to determine any problems with current formulations and to develop possible new formulations. The bulk nitration route proposed recently is a typical example (28).

(b) Extraction was noted by one contact as needing more study. In a kerosene context, the amount of extract may well present little problem in disposal and various chemicals are, or have been, made from middle distillate extracts - e.g. naphthalene from light cycle oils. A combination with hydrotreating may also be considered (108).

(c) Probably of most importance is the keeping abreast of developments by process competitors.

7.3 NICKEL CATALYST SPECIFIC

(a) The non-regenerability is by far the major concern and any viable approaches to increased sulphur and nitrogen tolerance should be explored. It is to be noted that such approaches could radically change the optimum reactor design to an ebullated or slurry type. This is not seen as a detriment and could well prove a plus. It is now used in benzene saturation in a number of plants (47)(98). Bartholomew considered oxidative regeneration worthy of development in 1982 and this study definitely concurs (6); but, there may be other options also to be considered.

(b) Without regenerability, increased sulphur and nitrogen tolerance would still be a major plus. This is true even if activity drops and higher temperatures are needed. (At higher temperatures the heat of hydrogenation would be much more useful.) But isomerization - lower cetane - and hydrogenolysis reactions and other safety concerns will need addressing at higher temperatures. This probably means the development of new catalyst formulations; hence, a relatively long development program.

(c) Initially, work on kerosenes is recommended with higher boiling material added with time. Emphasis needs to be on smoke point and aromatics, kerosene and cetane, and only later aromatics reduction in diesels.

(d) Trace impurity concerns other than sulphur and water must be addressed.

(e) Definition of prior hydrotreating parameters is needed but is of lower priority as the above work may well result in reducing its severity.

(f) Guard bed studies also fall into the same priority class - necessary but work on saturation catalyst per se should come first.

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APPENDIX A

NICKEL CATALYST HAZARDS

A.1 Hazardous Properties

A.1.1. Flammability

Nickel catalysts, though not dangerous commodities, have a kindling point of about 82°C depending on composition and manufacturer. Thus, conditions capable of generating temperatures in this range should be avoided.

The nickel catalyst used by CANMET, like most similar catalysts, was pre reduced at the factory and then a monomolecular layer of carbon dioxide formed to overcome most handling hazards. Special techniques are used when spent catalyst is dumped to avoid a fire hazard. A carbon dioxide layer can be laid down when the catalyst is to be reused. If this is not done, the catalyst should be kept moist.

A.1.2. Toxicology of Nickel

Although not conclusively established, there is growing evidence that nickel may be an essential element for humans. However, it has been confirmed that various forms of nickel do produce chronic dermatological, respiratory, endocrine and cardiovascular effects. Reproductive and developmental effects have been noted in animals, but have not been confirmed in humans. There is evidence both in humans and animals for the carcinogenicity of nickel, at least in some forms (31)(37)(72)(73)(94).

In terms of acute human toxicity of nickel and its compounds, nickel carbonyl probably presents an extreme hazard in cases of exposure. Acute nickel carbonyl poisoning may result in immediate and/or delayed symptomology. The lung is the primary target organ in both man and animals. The eight hour Occupational Exposure Limit is 0.05 ppm (or 0.34 mg/m^3) as Ni (37).

Nickel dermatitis and other dermatological effects of nickel have been documented in both nickel worker populations and the general public. Originally considered to be a problem of industrial hygiene, more recent studies suggest that non-occupational exposure to nickel containing commodities may present a significant problem to the general populace. Sources of dermatitis and associated effects include metallic nickel (solid, plated and alloyed) and nickel electroplating solutions.

Non-carcinogenic effects of nickel in the human respiratory tract have been established from studies of nickel workers in certain production or use categories who have been exposed to various forms of nickel. Although well established in animals, the cardiotoxic properties of nickel in humans is not well established. Analyses of nickel refinery workers suggest that cardiovascular disease is not a major risk associated with occupational exposure to nickel.

Exposure to nickel has been shown to cause both reproductive and development effects in experimental animals; however, such effects have not been documented in humans.

Apart from the toxicity of nickel carbonyl and the dermatological effects of nickel in various forms, the acknowledged carcinogenic effects of nickel, at least in some forms, are a major concern of the nickel producing and manufacturing industries. The strongest evidence of carcinogenicy is associated with refinery dust from pyrometallurgical processes. Excess risk of nasal and lung cancer has been reported for nickel refinery workers in Canada, The United Kingdom and Norway. Although nickel may be emitted in many forms, throughout the refining process, attention has been directed to nickel metal, nickel subsulphide (Ni_3S_2), nickel carbonyl, and nickel salts which may be emitted as aerosols from electrorefining operations.

According to the U.S. Environmental Protection Agency's classification scheme for evaluating carcinogens, only three compounds or mixtures of nickel compounds can currently be classified as either Group A (known human carcinogens) or B (probable human carcinogens) (33). Nickel refinery dust from pyrometallurgical nickel matte refineries is classified as Group A. Evidence suggests that nickel subsulphide is also in Group A. While there is inadequate evidence from epidemiologic studies with regard to evaluating the carcinogenicity of nickel carbonyl, there is sufficient evidence from animal studies to classify it as Group B. Some biochemical toxicological studies seem to indicate the nickel ion as a potential carcinogenic form of nickel and nickel compounds. Such a mechanism is not universally accepted at this time.

A.2 SAFETY PRECAUTIONS

A.2.1. Storage and Handling

Reduced nickel catalysts are normally stabilized against pyrophoricity. However, certain storage and handling precautions should be exercised to ensure safety.

Conditions capable of generating temperatures in the range of the kindling point should be avoided. Heat generated from reaction with excess moisture and air, combined with heat from an external source could raise the catalyst temperature to the initial range. Precautions to guard against these hazards include:

- store in a cool, dry place,
- keep away from heat or fire, and
- do not expose the catalyst to combustible vapours.

Allergic reactions to nickel metal are not common. However, to avoid reaction by personnel who are sensitive to the metal and to limit possible sensitization of others, minimum physical contact is recommended. Specifically, the following precautions should be mandatory:

- avoid inhalation of dust,

- avoid contact with eyes,
- avoid prolonged or repeated contact with skin, and
- wash thoroughly after handling.

A.2.2 Chemical Reaction

The principal chemical reactions of nickel which may introduce severe toxological implications include the generation of nickel carbonyl from metallic nickel and carbon monoxide.

To form the carbonyl, the metal must represent a high surface area. In effect then, a catalyst formulation is ideally suited for producing carbonyls. Favourable conditions include high partial pressures of carbon monoxide and temperatures in the range of 30 - 50°C.

The present of oxygen or water hinders the reaction, as does an oxide coating on the metal. Ammonia, hydrogen and small quantities of sulphur compounds in the carbon monoxide tend to increase the rate of formation of the carbonyl. The effect of sulphur compounds is surprising when their role as poisons for catalysts is recognized. However, H_2S, COS, C_4H_4S and even SO_2 have been cited as promoters of the reactions to form carbonyls.

In catalytic reactors the most likely time when carbonyl formation may occur is during start-up or shutdown, since these periods encompass the temperature range favourable for their formation. In shutting down, a catalyst should never be permitted to cool down to ambient temperatures in the presence of CO. Flushing with CO-free gas should be implemented when the temperature drops to 100 - 520°C, depending on pressure and CO concentration. For start-up the above precautions should be applied in reverse order.